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2.	Patent application number *(The Patent Office will fill in this part)*	0313617.3
3.	Full name, address and postcode of the or of each applicant *(underline all surnames)*	Patterning Technologies Limited Fujifilm House Boundary Way Hemel Hempstead Hertfordshire HP2 7RH
	Patents ADP number *(if you know it)*	8307966002
	If the applicant is a corporate body, give the country/state of its incorporation	GB
4.	Title of the invention	Transparent conducting structures and methods of production
5.	Name of your agent *(if you have one)*	
	"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	MATHYS & SQUIRE 100 Gray's Inn Road London WC1X 8AL United Kingdom
	Patents ADP number *(if you know it)*	1081001

		Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*
6.	If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number			

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8.	Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:* *a) any applicant named in part 3 is not an inventor, or* *b) there is an inventor who is not named as an applicant, or* *c) any named applicant is a corporate body.* *See note (d))*	YES

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Description	51
Claim(s)	9
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12. Name and daytime telephone number of person to contact in the United Kingdom

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DUPLICATE

Transparent Conducting Structures and Methods of Production

Introduction

The present invention relates to transparent conducting structures and more particularly to methods of producing transparent conducting structures.

Transparent conducting thin films in the form of inorganic and intrinsically conducting organic coatings, such as ATO, ITO, and polyaniline, are currently employed in a wide range of electro-optic devices that include electrodes for flat panel displays, electro-optic switches, and integrated opto-electronic circuits. The selected transparent conductor is generally deposited as a whole area coating and then subsequently patterned using conventional photolithographic patterning techniques in conjunction with liquid (i.e., HCl, etc.) or dry etchants (i.e., reactive ion beams or reactive ion plasmas including He, H_2, CH_4, O_2, HBr, Cl_2, etc.). It is also known that pulsed laser techniques can be used to both subtractively pattern, as well as, additively pattern such coatings. In all cases the nature of the patterning technique is either expensive due to the capital nature of the equipment being used when considering sample throughput or requires many processing steps that are labour intensive and affect the useable yield. It is known that screen-printing can be used to produce patterned transparent conductors but this technique has limitations with respect to feature resolution and minimum thickness.

In its preferred forms, the present invention seeks to address the limits of the processes outlined above by considering thin film materials, device configurations, and advanced printing processes that lend themselves to direct patterning.

There is therefore provided as a first aspect of the invention, an electrical conductor having a region comprising transparent electrically conductive material having dispersed therein electrically conductive particles formed from material having a higher conductivity than the transparent material. This takes advantage of the much lower electrical resistivity of the electrically conducting particles and the high optical transmissivity of the transparent (though less conducting) particles and combines them to give a highly transparent, highly conducting transparent conductor.

This conductor design opens up the possibility of achieving the best of metal conductors and transparent conductors

The transparency of that region of the conductor may be preferably greater than 70%, preferably greater than 80%, at 550 nm wavelength. For the highest performance end of the flat panel display market, a very high transparency at 550 nm may be required. Assuming all of the metal nanoparticles promote an increase in luminous absorption, then the transmissivity would be expected to reduce as metal particles are added to the transparent material. However, given the multiple particle stacking nature of thin film, some of the metal particles will be aligned directly above other metal particles thereby reducing the effective absorption due to a reduced absorption capture cross-section potentially raising the effective luminous transmissivity.

The flat panel displays may be used in laptops, mobile phones, hand-held personal processors and electronic games which require very high optical transmissivity across the luminous waveband.

The conductive particles preferably comprise nanoparticles. These conductive particles are preferably of uniform or non-uniform size, but preferably have a mean size less than 1000 nm. The conductive particles preferably have a mean size less than 100 nm, more preferably less than 20 nm.

The ratio of the size of the conductive particles to the size of particles of the transparent material may be preferably equal to or less than 1:1, preferably less than 0.5:1.This may be because the ratio of the metal particle size to the transparent conductor particle size ~~may be an important factor in optimising the electrical and optical performance of the~~ mixed particle film. This may be because equal sized particles will take up a larger volume for the same number of interparticle connections. However. if the metal particle may be of a size that permits contact between transparent conductor nearest neighbours and the associated metal particles, then the volume of metal may be reduced over that area for identical particle size and the effect of direct absorption of light may be reduced

in the ratio of the volumes. There may be a specific relationship between the size of the metal particle to the transparent conductor on purely geometrical grounds if all surfaces are to touch, which from geometrical and mathematical considerations suggests that the metal particle diameter (assuming a spherical particle) could be of order 0.42 times the diameter of the transparent conductor. This suggests that, for instance, a transparent conducting particle of size 18 nm could be combined with a metal particle size of 7.56 nm.

The transparent material may be preferably selected from the group consisting of a transparent conductive oxide and a transparent polymer such as:

- Inorganic transparent conducting oxides [ATO, TO, ITO, FTO, ZnO, $SrCu_2O_2$, etc.]
- Organic [Pedot-PSS, Polyaniline, etc.]
- Organically modified ceramics [Metal alkoxides, etc.]

The conductive particles preferably comprise metal particles, more preferably at least one of silver, gold, copper, aluminium, tin, zinc, lead, indium, molybdenum, nickel, platinum and rhodium particles.

The ratio of the number of particles of the transparent material to the number of conductive particles may be preferably substantially uniform throughout the conductor. This can provide a minimum volume for a maximum nearest neighbour contact density for each particle type. It may be possible to construct this packing structure in a manner that permits metal-to-transparent conductor particle contact with or without transparent conductor-to-transparent conductor contact. In order to achieve the maximum charge transfer, a metal particle may be selected that is small enough to reside interstitially between the close-packed transparent conductor particles whilst still contacting each transparent conductor particle, while permitting the transparent conductors also to touch each other. This could provide a means of combining metal and transparent conductor particles in such a manner that maximum conductivity and transmissivity can be achieved in a single coating that would not be achieved from a coating containing only one particle type.

This ratio of the number of particles of transparent material to the number of conductive particles may be preferably equal to or greater than 4:1. If each particle is spherical in shape and of the same diameter then it could be expected that one metal particle would contact 4 transparent particles, thus providing more efficient interaction between particle types.

Within this region, the ratio of the number of particles of transparent material to the number of conductive particles may be preferably locally varied in order to provide sub-regions with different conductivity, optical transmissivity and/or thickness.

Preferably, said region of the conductor has a sheet resistance of less than 800 Ω per square. A mixed ink serves the need to be able to print whole area and patterned transparent conductors that exhibit a sheet resistance of less than 800 Ohms per square with a transparency of at least 85% at 550 nm wavelength (which may be central to the luminous waveband).

Preferably, said region comprises a single layer of transparent material having said conductive particles dispersed within. In attempting to achieve this in a single ink, it may be possible to consider combining a highly conductive particle with a transparent conducting particle to introduce a small number of conduction centres in a p-type semi conducting sea. In order to achieve the maximum charge transfer, it may be necessary to select a metal particle that may be small enough to reside interstitially between the close-packed transparent conductor particles whilst still contacting each and permitting the transparent conductors to touch each other also. This provides a means of combining metal and transparent conductor particles in such a manner that maximum conductivity and transmissivity can be achieved in a single coating that would not be achieved from a coating containing only one particle type.

Preferably, in said region, the conductive particles are located between respective layers of transparent material. The transparent conducting material portion of a multilayer can be continuous whereas a metal layer portion of the multilayer can be deposited in a selective

fashion so as to promote the equivalent of higher conductivity links within a continuous sea of transparent conducting material but permitting the actual pixel areas to remain higher in luminous transmissivity.

If the luminous transmissivity is reduced by some factor, then it may be possible to construct a trilayer (though it could be binary or higher) transparent electrode using, for instance, drop-on-demand ink jet printing that comprises the following layer sequences:

- TCO/Metal/TCO
- TCO/Metal/TCO/Metal/TCO

The resulting resistance of a three-layer transparent conducting material only structure may be of the order of 6,600 Ohms, whereas the equivalent resistance of this trilayer vertically stacked structure may be of the order of 900 Ohms. The conductivity of this sort of trilayer is therefore considerably greater than three layers of transparent conducting material only.

Said region preferably further comprises translucent spheres embedded within the transparent material.

Preferably, at least one conductive track provides a source or sink for electrical charge transport to and from said region. The continuous nature of a track surrounding a window provides a means of achieving very high conductivity to provide a source or sink for electrical charge transport into and out of the transparent conducting material that may be deposited in each window. By using particulate or molten droplet metal, the film thickness may be the same or increased relative to an otherwise equivalent transparent conductor for the same geometric area, but with the differing thickness metal, the resulting reduction in resistance may be by a factor of the order of 136 (same film thickness) and 408 (increased thickness), providing means for limiting the voltage drop along conductor length.

The track may be preferably of lower transparency than said region at 550 nm wavelength since it has the required conductivity. The transparent conductor used to provide the conductive window contact can deliberately possess a lower electrical conductivity since the length over which the electronic charge must travel may be very much reduced. This opens up the potential of providing a much higher optical transparency as a result of the lower density of charge carriers since according to electro-magnetic theory; high conductivity and high optical transmissivity are mutually exclusive because photons are strongly absorbed by the high density of charge carriers that promote electrical conductivity.

The track preferably has a width equal to or less than 50 microns. It may be necessary to strike a balance between the conductivity of the track and its visibility. A track of 3mm thickness may be sufficient for a large area flat panel display, but for many applications, such as high information content, high resolution hand-held displays, a track of 50 microns or less may be necessary in order to enable the information to be efficiently seen.

There may be preferably provided an electronic device comprising at least one electrical conductor as described above. Indeed, numerous applications may benefit from the application of transparent conducting thin films, including

- 2- and 3-dimensional periodic structures
- Electrochromic "Smart" windows: [patterned and whole area]
- Electronic blinds and large area shutters
- Electro-optic micro shutters: [LCD, ferroelectric, electrochromic]
- Electro-optic switches: [organic and inorganic]
- Flat panel displays: [Low and high resolution, current and field switched active and passive addressing]
- Integrated optical devices: [modulators, detectors, spectrum analysers, converters, spatial light modulators]
- Light emitting diodes and lasers: [organic, polymeric, inorganic]
- Micro sensors: [discrete devices and arrays for gas sensing]
- Non-linear optical devices: [organic and inorganic active waveguides]
- Photovoltaic cells and switches: [organic and inorganic]

- Touch-sensitive switches: [capacitive]
- Transparent antennas
- Transparent heaters and ice demisters: [large area and integrated device micro heaters]
- Transparent micro heaters

The electronic device may comprise a p-type transparent electrically conductive electrode and an n-type transparent electrically conductive electrode, each preferably comprising a conductor as described above. The production of both n- and p-type conducting transparent electrodes opens up the possibility of creating p-n junctions based on the printing of p-type and n-type materials. This can be achieved either as conventional vertical stacked structures or as a single layer comprising a homogeneous distribution of n- and p-type material in close proximity to create novel electronic structures.

A second aspect of the present invention provides a method of fabricating an electrical device, comprising printing on a substrate an electrical conductor comprising transparent electrically conductive material having dispersed therein electrically conductive particles formed from material having a higher conductivity than the transparent material.

Preferably, a fluid comprising both the electrically conductive particles and the transparent material may be printed on the substrate. Alternatively, a first fluid comprising the transparent material and a second fluid comprising the electrically conductive particles are printed on said substrate. The fluids are preferably printed using respective printheads.

The first and second fluids may be printed sequentially.

Electrically conductive particles are preferably selectively printed so as to form regions of locally increased density and/or thickness on the substrate, such as conductive contacts or tracks or any other pattern or formation that increases the efficiency of the conductor. It possible to use two independent printheads that are placed back-to-back or are combined in a suitable locating jig such that droplets ejected from each printhead are co-incident on

the surface area to be coated. This means that the properties of adjacent segments of the same electrical conductor can be modified so as to achieve local changes in electrical conductivity, optical transmissivity, and thickness.

The transparent material may be printed over previously printed electrically conductive particles.

The electrically conductive particles may be printed over previously printed transparent material. In this way, it may be possible to print directly the required metal type in micro or nanoparticle form as a specific pattern onto the transparent material.

On the other hand, the electrically conductive particles may be deposited directly on to the substrate.. It may be also possible to apply the particles directly onto a surface that forms part of a device.

The first and second fluids may alternatively be printed simultaneously.

The printing of the transparent material and the electrically conductive particles may form a printed hybrid, and the method may further comprise annealing the printed hybrid. The manner in which nanoparticles contained in an ink droplet, ejected from a drop-on-demand ink jet printhead, come together on the receiving surface, coupled with the nature of any post-treatment (e.g., laser or rapid thermal annealing) may be of significant importance in producing a high mobility device

The whole structure can be thermally annealed to effect good electrical connectivity and electrical performance between the two materials without impairing the very high optical quality. For instance, the conductivity of the material may be designed to provide good charge mobility but only over a limited distance; that may be to the nearest bus bar.

A third aspect of the present invention provides the use, in the manufacture of an electrical conductor comprising transparent electrically conductive material, of metallic nanoparticles.

The nanoparticles are preferably dispersed within the transparent material to improve conductivity thereof. Nanoparticles are more easily distributed around a material than larger particles, thus improving overall conductivity as long as the nanoparticles are conductive and have means for interacting with other conducting substances.

According to a fourth aspect of the present invention, there is provided an electrical conductor comprising transparent spheres embedded within transparent electrically conductive material. An approach to creating transparent conductive devices may be to separate the electrical performance from the optical performance by virtue of combining two independent materials that offer the best for both properties whilst still retaining adequate electrical conductivity in the optical material in order to achieve the transparent electrode behaviour.

The mixed nanoparticle ink can include optical micro and sub-micro spheres that are optically clear, such as silica or polyethylene structures. The micro spheres, which could be conducting, semiconducting, or insulating, enhance luminous transmissivity and also influence the geometrical dispersion of the emitted light, as well as promote improved durability and wear resistance. The spheres preferably have a mean diameter of less than 10 microns. The spherical form aids in packing of the particles and the small size aids in the efficient distribution of the particles and opens up several avenues of application of the spheres onto a substrate or into the transparent material.

The conductor preferably comprises, between the transparent electrically conductive material and a substrate, a layer of transparent material to which the spheres are secured. It may be possible for the nano or micro spheres to be added to a printed transparent conductor before it has been dried so that the spheres are retained in the material. It may be also possible for the nano or micro spheres to be added to a surface to provide a distribution of dried spheres that would then be embedded by printing a second transparent conductor ink, such as a metal alkoxide sol or intrinsically conducting polymer, that would coat around the spheres provide mechanical binding and electrical transport.

Preferably, the spheres and the layer of transparent material are substantially optically matched. The in-fill material can be used to provide optical matching to the substrate media in order to minimise reflection losses. Once this filling has been completely dried than the whole area coating of the transparent conducting material can be completed

The transparent material may be preferably selected from the group consisting of a transparent conductive oxide and a transparent polymer, for example:

- Inorganic transparent conducting oxides [ATO, TO, ITO, FTO, ZnO, $SrCu_2O_2$, etc.]
- Organic [Pedot-PSS, Polyaniline, etc.]
- Organically modified ceramics [Metal alkoxides, etc.]

The spheres are preferably formed from one of conductive, semiconductive or insulating material.

A fifth aspect of the present invention provides a method of fabricating an electrical device, comprising printing on a substrate an electrical conductor comprising transparent electrically conductive material and transparent spheres.

Preferably, a first fluid comprising the transparent material and a second fluid comprising the spheres are printed on said substrate. The nano or micro spheres may be added to a printed transparent conductor before it has been dried so that the spheres are retained in the material. The nano or micro spheres may be added to a surface to provide a distribution of dried spheres that would then be embedded by printing a second transparent conductor ink, such as a metal alkoxide sol or intrinsically conducting polymer, that would coat around the spheres provide mechanical binding and electrical transport.

The fluids are preferably deposited using respective printheads.

The first and second fluids may be deposited sequentially. As mentioned above, the nano or micro spheres may be added to a surface to provide a distribution of dried spheres that would then be embedded by printing a second transparent conductor ink, such as a metal alkoxide sol or intrinsically conducting polymer, that would coat around the spheres provide mechanical binding and electrical transport. Sequential deposition may be therefore required.

The transparent electrically conductive material may be initially printed on to the substrate, and the spheres may be subsequently deposited on the transparent material before complete drying thereof so that the spheres become embedded within the transparent material. This provides mechanical binding and electrical transport, as required.

A second transparent material may be initially deposited on to the substrate, the spheres being deposited on that transparent material before complete drying thereof so that the spheres are retained by that transparent material, the transparent electrically conductive material being subsequently deposited between the retained spheres. This can provide another method of ensuring that the particles are properly embedded in the transparent material for the reasons outlined above.

The second transparent material may be cured using electromagnetic radiation prior to the deposition of the transparent electrically conductive material. This can help to keep the transparent materials separate and the particles embedded in order to retain desired properties of the respective materials.

The printing of the transparent material and spheres may form a printed hybrid, the method preferably further comprising annealing the printed hybrid. The whole structure may be thermally annealed to effect good electrical connectivity and electrical performance between the two materials without impairing the very high optical quality.

A sixth aspect of the present invention provides the use, in the manufacture of an electrical conductor comprising transparent electrically conductive material, of

transparent spheres. The spheres may be embedded within the transparent material to improve the photon transmissivity of the conductor.

The spheres may be embedded within the transparent material to improve durability and/or wear of the conductor.

A seventh aspect of the present invention provides an electrical conductor comprising transparent electrically conductive material and at least one conductive track formed from nanoparticles and providing a source or sink for electrical charge transport to and from the transparent material.

The continuous nature of the track provides a means of achieving very high conductivity to provide a source or sink for electrical charge transport into and out of the transparent conducting material, which may be deposited in awindow at least partially surrounded by the track.

The nanoparticles are preferably of uniform or non-uniform size, and have a mean size less than 1000 nm. The nanoparticles more preferably have a mean size less than 100 nm, preferably less than 20 nm. The small size of the nanoparticles enables them to be applied to a substrate, for instance via an ink from a printhead, and for them to be more easily distributed in a thin film over the substrate or other surface. Furthermore, given the use of nanotectics, a focused laser that permits impact dynamic and spreading/coalescence equilibrium to be achieved can be employed to reflow the printed metal nanoparticles. This opens up the possibility of printing a wide variety of such metal nanoparticles on to temperature stable and temperature sensitive substrate media and to employing a much wider range of metal elements and alloys using particles in the range 1 to 10 nm.

The transparent material may be preferably selected from the group consisting of a transparent conductive oxide and a transparent polymer, for example;

- Inorganic transparent conducting oxides [ATO, TO, ITO, FTO, ZnO, $SrCu_2O_2$, etc.]

- Organic [Pedot-PSS, Polyaniline, etc.]
- Organically modified ceramics [Metal alkoxides, etc.]

The nanoparticles are preferably metallic, and more preferably at least one of silver, gold, copper, aluminium, tin, zinc, lead, indium, molybdenum, nickel, platinum and rhodium nanoparticles. These are high conductivity metals that could be considered for the production of conductive windows, wells, and constraining features that can be filled with an inorganic transparent conducting oxide (TCO) or an organic transparent conductor (OTC) whether doped, defect-induced, or intrinsically conducting. These conductive particles are preferably of uniform or non-uniform size, but preferably have a mean size less than 1000 nm. This opens up the possibility of printing a wide variety of such metal nanoparticles on to temperature stable and temperature sensitive substrate media and to employing a much wider range of metal elements and alloys using particles in the range 1 to 10 nm. Hence, the conductive particles preferably have a mean size less than 100 nm, more preferably less than 20 nm.

The conductor preferably has a transparency greater than 70%, preferably greater than 80%, at 550 nm wavelength. For the highest performance end of the flat panel display market that a very high transparency at 550 nm may be desirable.

The track and the transparent material may partially overlap. Overlapping the track and the transparent material may aid the efficiency of the source or sink for electrical charge into and out of the transparent material.

The conductor preferably comprises a plurality of conductive tracks at least partially surrounding the transparent material. This affords the same advantages as above.

The track may directly contact the transparent material. Alternatively, the conductor may comprise further, electrically conductive material disposed between the track and the transparent material. The quality of the metal contact surrounding each contact window well may be enhanced by printing the edge of the well using a different ink, such as a metal alloy, cermet, or mixed particle ink, that provides controlled wall wetting, better

electrical contact matching and lower contact resistance, and provides a means of controlling the intermetallic behaviour and mechanical strength at the interface between the metal conductor, the contact window edge, and the transparent conducting material that may be deposited within it.

It is possible to fill a rectangular track well with a transparent conducting material that is electrically connected to the conductive walls of the well. This gives low sheet resistance because the connecting conductive links bridging the two long conductors effectively short-circuit the material that may be deposited between them.

The conductor may be preferably disposed on a transparent substrate. This may be so that the entire structure may be as transparent as possible, while retaining conductivity.

The conductor preferably comprises further transparent material located between the substrate and the transparent electrically conductive material.

The track may be of lower transparency than the transparent material at 550 nm wavelength. The track preferably has a width equal to or less than 100 microns, more preferably equal to or less than 50 microns.

An eight aspect of the present invention provides a method of fabricating an electrical conductor, comprising selectively depositing on a substrate a fluid comprising electrically conductive particles, causing the deposited particles to form at least one continuous, discrete conductive track, and forming at least one region of transparent electrically conductive material on said substrate, the track providing a source or sink for electrical charge transport to and from the transparent material. The continuous nature of the metal surrounding each window can provide a means of achieving very high conductivity to provide a source or sink for electrical charge transport into and out of the transparent conducting material.

The track may be formed by at least one of sintering, melting and annealing. Given the use of nanotectics, a focused laser, located adjacent to the point of droplet impact or at some controlled distance from the point of droplet impact (including the use of laser

scanning and spatial light modulation) that permits impact dynamic and spreading/coalescence equilibrium to be achieved, can be employed to reflow the printed metal nanoparticles.

The region of transparent material may be formed by selectively printing said transparent material on said substrate, preferably using a drop on demand printing technique. Since the conducting line width may be so large compared to the printed feature resolution, it may be possible to print directly the required metal type in micro or nanoparticle form as a specific pattern that includes an integral well within a continuous conductor. The printed metal track with discrete via-holes or contact windows in it may then be thermally treated using a laser or rapid thermal process in a controlled atmosphere so as to create an amorphous or other preferred crystalline state whilst retaining the purity of the original metal particles. The width of the walls parallel to the direction of the conductive track that may be used to address individual display pixels may be printed at a width that cannot be discerned by eye at the correct viewing distance for the display device to be produced. The continuous nature of the metal surrounding each window provides a means of achieving very high conductivity to provide a source or sink for electrical charge transport into and out of the transparent conducting material that may be to be deposited in each window.

The manner in which nanoparticles contained in an ink droplet, ejected from a drop-on-demand ink jet printhead, come together on the receiving surface, coupled with the nature of any post-treatment (e.g., laser or rapid thermal annealing) may be of significant importance in producing a high mobility device.

A transparent conducting window may be formed directly in the reflowed/annealed/recrystallised metal printed conductor or feature in a manner that is dependent upon the scale of the feature to be produced. For example, a 3 mm wide conductor and a 50 micron wide conductor may provide a transparent conducting window adjacent to a display pixel as part of an addressing line in a large area flat panel display for the 3 mm wide conductor or a high information content high resolution hand-held display for the 50 micron wide conductor.

The transparent material may be deposited over the conductive tracks.

The track may be formed from electrically conductive material which, when oxidised, becomes at least partially transparent, the region of transparent material being formed by selectively oxidising portions of said track. Thus, there may be used a single printing ink that comprises a metal particle that when oxidised becomes a highly transparent but electrically conducting material.

A self-assembled non-wetting monolayer can be deposited for example using drop-on-demand ink jet printing, and be patterned in a step-and-repeat manner using an integrated UV Lamp patterning or Laser digital pattern transfer to create wetting and non-wetting regions on the surface. A second transparent conductor ink may then be delivered to the surface using ink jet printing that segregates to the wetting lands to produce the required transparent conductor layout, with the patterning defining monolayer material being removed using chemical means.

The electrically conductive material may comprise a metal with a lower melting temperature than that of the transparent material. Metals have low resistivity (they are highly conducting) and low melting temperature metal particles are more easily used in nanotechnics. This provides a means of limiting the voltage drop along such a conductor when employed in rigid or flexible large area flat panel displays or photovoltaic cells/panels/sheets. As pure metal electrical resistivity can be achieved in the laser melted or rapid thermally processed (RTP) ink jet patterned features, the resistance of a common conductor geometry fabricated using low melting temperature metal particles will be reduced when compared with the best conventionally deposited transparent conductor resistivity depending on the metal chosen.

The track and the region of transparent material are preferably formed using nanotechnics. Given the use of nanotectics, a focused laser that permits impact dynamic and spreading/coalescence equilibrium to be achieved can be employed to reflow the printed metal nanoparticles. This opens up the possibility of printing a wide variety of

such metal nanoparticles on to temperature stable and temperature sensitive substrate media and to employing a much wider range of metal elements and alloys using particles in the range 1 to 10 nm.

The fluid may be preferably selectively deposited using a drop on demand printing technique. This may be a very precise way of depositing the fluid where it may be required in order to print the desired patterns.

The fluid may be deposited within grooves formed on the substrate, preferably so as to partially fill the grooves. A glass plate which has been coated with a self-assembled monolayer (SAM) may provide a highly non-wetting surface. A laser may be scanned over the plate surface to define a series of grooves in the near surface and plate surface, which are below the detection limit of the eye and form a set of containment trenches. The grooves, which can be produced using other methods, can be in a single direction (x or y) or in orthogonal directions (x and y) where the cross-over points provide connectivity between the both axes. The resulting grooves are filled with fluid which can be achieved using precision spraying or drop-on-demand ink jet printing, where the wetting nature of the groove wall causes the ink to flow into the etched trench leaving the surface free of ink because of the differential nature of the surface energy in the groove and that related to the non-wetting SAM coating on the exposed surface between the grooves. The resulting solidified metal in-fill preferably does not completely fill the groove in order that the transparent conducting coating can flow into the groove and provide a direct connection on to the metallic bus bar

The grooves may be formed in a coating formed on the substrate. A coating may be more readily adapted to have grooves etched into it, for example.

The grooves may be formed by laser ablation. Laser ablation may selectively remove the coating material thereby producing the required shallow groove in a material that can be electrolytically plated to provide the high conductivity copper bus bar structure whilst still retaining a very high open area that may be devoid of any undesired material.

The track may formed subsequent to the formation of the at least one region of transparent electrically conductive material on said substrate. For example, screen printed metal tracks may be printed onto a transparent conductor to provide a means of providing an electric current to the transparent conductor making use of a low resistance electrical bus bar/conductor that may be not transparent.

A ninth aspect of the present invention provides a method of fabricating an electrical conductor, comprising selectively forming on a substrate at least one conductive track defining a window at least partially surrounded by said track, and subsequently using the technique of drop-on-demand printing to deposit transparent electrically conductive material within said window, the track providing a source or sink for electrical charge transport to and from the transparent material.

The track may be formed on the substrate using a lithographic printing technique. A hybridisation of offset lithographic and drop-on-demand ink jet printing may be used to produce the transparent conducting element required.

The track may be formed on the substrate using a plating technique. The offset lithographic process may use a 3 micron thick electroless plating insulating seed layer. The printed seed layer may be immersed in an electroless plating bath and a thin thickness of copper metal may plated on to the seed layer. The copper thickness may modifies the actual bus bar and tram line spacing by virtue of the fact that the electroless plating may be deposited on all exposed surfaces of the seed layer, hence, for example, a 10 micron wide seeding layer track will increase to 12 micron and the adjoining transparent window width, located between the opaque metal tram lines, will be reduced to 98 microns for a 1 micron electroless plated copper thickness. The resulting electroless plated copper film may possess a transparent low window bus bar resistance.

The track preferably provides a containment well for the transparent material. Two conductors may be spaced, say, 1 mm apart and may be connected at the ends to form a rectangular containment well. Electrically the connection nodes are such that the two

separated conductors behave as if they were a single conductor of double width and the same thickness, improving the effective conductivity.

The rectangular well may be filled with a layer of transparent conducting material which is electrically connected to the conductive walls of the well. In this case the sheet resistance may be the same as otherwise because the connecting conductive links bridging the two long conductors effectively short-circuit the material that may be deposited between them. This can ensure that charge generated in the centre of the well can reach the conductor and be swept away thereby acting as a continuous transparent conducting rectangular window.

A plurality of layers of transparent material may be deposited within said window.

Examples of processes of coating and patterning transparent screens which will be discussed further are:

- Continuous ink jet printing
- Digital off-set lithography
- Drop-on-demand ink jet printing
- Electrophotographic printing
- Electrostatic printing
- Flexographic printing
- Gravure off-set lithography
- Ionographic printing
- Laser xerographic printing
- Magnetographic printing
- Soft lithography stamp transfer
- Stencilling
- Touch transfer (ink nib process)

Existing printed transparent conductors possess a uniform transparency and conductivity over the surface area of the as-etched and post-treated (where necessary) feature. This

means that a specific length and cross-sectional profile of transparent conductor will exhibit an electrical resistance dictated by the resistivity of the thin film used in its construction. For specific application of transparent conducting thin films where the whole area does not need to be transparent, such as in the electrical contacting of flat panel display pixels, it is possible to design the contact tracks so as to create a region that is transparent and a region that is of a lower transparency or is opaque but that possesses a higher conductivity. The functionality of the contacted device is dictated only by the transparent window with the other region providing a means of introducing or removing electronic charge.

Any feature in one aspect of the invention may be applied to other aspects of the invention, in any appropriate combination. In particular, method aspects may be applied to apparatus aspects, and vice versa.

Preferred features of the present invention will now be described, purely by way of example, with reference to the accompanying drawings, in which:

Figure 1 shows the laser or rapid thermal annealing of an ink printed onto a substrate;
Figure 2 shows a metal and transparent conductor ink layer;
Figure 3 shows a branched conductor;
Figure 4 shows a ladder conductor;
Figure 5shows a stepped conductor;
Figure 6 shows a metal and transparent conductor layer with the metal in ink droplet form;
Figure 7 shows a double laser or rapid thermal annealing process;
Figure 8 shows a simplified containment channel;
Figure 9 shows the containment channel with copper electroless plating;
Figure 10 shows a containment channel with an optically matched polymer layer;
Figure 11 shows the top view of an isolated containment channel;
Figure 12 shows an interdigitated containment channel structure;
Figure 13 shows a simple view of a metal and transparent conductor layer with overlap;
Figure 14 shows etched and filled grooves on a glass plate;
Figure 15 shows a trilayer conductor containing particles;

Figure 16 shows a mixed ink conductor; and

Figure 17 shows the packing structure of different sizes of metal and transparent particles.

The present invention takes advantage of the much lower electrical resistivity of such low melting temperature metal particles, as zinc, to provide a low resistance conductor that has, as an integral feature, contact windows into which can be deposited any material including, in this case, a transparent conductor.

The rapid thermal or laser reflowed material can be further smoothed using a hot air/inert gas jet or shower once the initial particle coalescence into a continuous film has been achieved.

Figure 1 shows an ink 2 containing metal particles 3 which has been printed onto a substrate 4 and then laser annealed using laser 5 or rapid thermally annealed using a high power LED 5, to promote coalescence and interdiffusion for better charge transport.

Other possible low melting temperature metals include but are not limited to:

Metal	**Symbol**	**Resistivity Ω-cm at "X"^{o}C**	**Conventional Melting Temperature ^{o}C**
Indium	In	8.37×10^{-6} at 20^{o}C	156.6
Lead	Pb	20.65×10^{-6} at 20^{o}C	327.5
Tin	Sn	11.0×10^{-6} at 0^{o}C	231.97
Zinc	Zn	5.92×10^{-6} at 20^{o}C	419.58

Given that the pure metal electrical resistivity can be achieved in the laser melted or rapid thermally processed (RTP) ink jet patterned features (some practical limit due to processing conditions will exist but it serves as an illustration of the potential benefit to use the bulk figure) it is expected that the resistance of a common conductor geometry fabricated using low melting temperature metal particles will be reduced by a factor of the order of 9 [Pb] to 33 [Zn] when compared with the best conventionally deposited transparent conductor resistivity (magnetron sputtered: 2×10^{-4} Ω-cm) dependent upon the

metal chosen. This ratio can be further increased by deliberately making the metal track geometry thicker. For example, a film thickness of zinc relative to the transparent conductor being increased by a factor of 3 results in a reduction in resistance for the same geometric area, but with the thicker metal, of a factor of 99. This provides a means of limiting the voltage drop along such a conductor when employed in rigid or flexible large area flat panel displays or photovoltaic cells/panels/sheets.

The transparent conductor used to provide a conductive window contact can deliberately possess a lower electrical conductivity since the length over which the electronic charge must travel is very much reduced. This opens up the potential of providing a much higher optical transparency as a result of the lower density of charge carriers since according to electro-magnetic theory; high conductivity and high optical transmissivity are mutually exclusive because photons are strongly absorbed by the high density of charge carriers that promote electrical conductivity. It is understood that for the highest performance end of the flat panel display market that a transparency at 550 nm of over 90%, preferably over 95%, (i.e. nearly completely transparent, rather than just translucent) is essential.

It is possible to expand the potential of the above conductor by considering the melting behaviour of metallic nanoparticles. It is known that for very small particles of order a few nanometres, it is possible to melt such particles at temperatures much lower than that required to melt a bulk quantity of the same metal due to surface tension effects (large surface-to-volume ratio). This opens up the possibility of achieving the best of metal conductors and transparent conductors using a dual drop-on-demand ink jet or alternate hybrid printing process.

Given the use of nanotectics, it is anticipated that a focused laser, located adjacent to the point of droplet impact or at some controlled distance from the point of droplet impact (including the use of laser scanning and spatial light modulation), which permits impact dynamic and spreading/coalescence equilibrium to be achieved, can be employed to reflow the printed metal nanoparticles. This opens up the possibility of printing a wide variety of such metal nanoparticles onto temperature-stable and temperature-sensitive substrate media and of employing a much wider range of metal elements and alloys using

particles in the range 1 to 10 nm. Examples of high conductivity metals that could be used for the production of conductive windows, wells, and constraining features that can be filled with an inorganic transparent conducting oxide (TCO) or an organic transparent conductor (OTC) whether doped, defect-induced, or intrinsically conducting are:

Metal	Symbol	Resistivity Ω-cm at "X" ^{o}C	Conventional Melting Temperature ^{o}C
Aluminium	Al	2.5×10^{-6} at 0^{o}C	660.46
Copper	Cu	1.55×10^{-6} at 0^{o}C	1,084.88
Gold	Au	2.05×10^{-6} at 0^{o}C	1,064.43
Molybdenum	Mo	2.05×10^{-6} at 0^{o}C	2,623.00
Nickel	Ni	6.2×10^{-6} at 0^{o}C	1,455.00
Platinum	Pt	9.81×10^{-6} at 0^{o}C	1,769.00
Rhodium	Rh	4.3×10^{-6} at 0^{o}C	1,963.00
Silver	Ag	1.47×10^{-6} at 0^{o}C	961.93

For example, a particulate or molten droplet of silver is used and the film thickness relative to an otherwise equivalent transparent conductor of electrical resistivity, ρ, of 2×10^{-4} Ohm-cm is left the same or is increased by a factor of 3. The resulting reduction in resistance for the same geometric area and same or higher metal thickness will be by a factor of the order of 136 or 408, respectively, providing an even greater means of limiting the voltage drop along the conductor length.

Whether the above conductor is based on a low or high melting temperature metal, a transparent conducting window can be created directly in the reflowed/annealed/recrystallised metal printed conductor in a manner that is dependent upon the scale of the conductor feature to be produced. For example, 3 mm wide conductors and 50 micron wide conductors serve the purposes of providing transparent conducting windows adjacent to display pixels as part of an addressing line in a large area flat panel display or a high information content high resolution hand-held display, respectively.

Figures 2 shows metal 20 (for example a micro particle metal 24) and transparent 30 layers on a single substrate 10. The overlapping region 40 provides electrical contact between the two types of layer. Figure 2a shows a side view and Figure 2b shows a top view of a "Dual Stripe Conductor Pattern", which is called such because there is a stripe of each of the two materials. Several other patterns using these materials may be created such as the "Branched" Conductor of Figure 3 with metal layer 20 and several separated transparent layers 35. The transparent layers may be separated with further conductor layers 20. Figures 4 show a "Ladder" Conductor with conductor layers 20 on substrate 10. As can be seen from the top view of Figure 4a, the conducting layers are made up of two parallel lines joined intermittently with further "rungs" of the ladder shape. The space between the rungs is filled with the transparent material 30, as can be seen in the side view in Figure 4b. Figures 5 show the "Stepped" Conductor. The top view of Figure 5a is similar to the "Ladder" Conductor shape. The difference between the "Ladder" and "Stepped" Conductors is that the conducting layer 20 has a step 25 (seen in Figure 5b) which is in the transparent layer 30 and provides greater electrical connection between the two materials.

Since the conducting line width is large compared to the printed feature resolution, which is, for instance, 50 microns, it is possible to print directly the required metal type in micro- or nanoparticle form as a specific pattern that includes an integral well within a continuous conductor. The printed metal track with discrete via-holes or contact windows therein is then thermally treated using a laser or rapid thermal process in a controlled atmosphere so as to create an amorphous or other preferred crystalline state whilst retaining the purity of the original metal particles. The width of the walls parallel to the direction of the conductive track that are used to address individual display pixels are printed at a width that cannot be discerned by the eye at the normal viewing distance for the display device. The continuous nature of the metal surrounding each window provides a means of achieving very high conductivity to provide a source or sink for electrical charge transport into and out of the transparent conducting material that is deposited in each contact window well.

Depending on the metal reflow conditions, it is possible to influence the geometry of the contact window well wall so as to eliminate the possibility of poor wall wetting particularly at the base of the wall, which if poorly wet would lead to the classic "mouse hole" effect.

Due to the resolution of the printing process relative to the large feature size it is possible to enhance the quality of the metal contact surrounding each contact window well by printing the edge of the well using a different ink, such as a metal alloy, cermet, or mixed particle ink, which provides controlled well wall wetting, better electrical contact matching and lower contact resistance, and which provides means of controlling the inter-metallic behaviour and mechanical strength at the interface between the metal conductor, the contact window well edge, and the transparent conducting material that is deposited within the well.

The large feature size also makes it possible to consider a wide range of printing methods to produce the required conductor pattern at a reasonable film thickness when dried and laser- or RTP- reflowed/annealed/recrystallised. Examples of suitable printing methods are:

- Continuous ink jet printing
- Digital plateless off-set lithographic printing
- Digital transfer plate off-set lithographic printing
- Droplet ejection (not ink jet)
- Dry toner printing
- Electrophotographic printing
- Electrostatic printing
- Flexographic printing
- Focussed acoustic energy lens less drop-on-demand ink jet printing
- Gravure printing
- Ionographic printing
- Laser xerographic printing
- Magnetographic printing

- Molten metal drop-on-demand ink jet printing
- Piezoelectric drop-on-demand ink jet printing
- Pin transfer
- Screen printing, especially for thin film transfer
- Soft contact stamping
- Sublimation printing
- Thermal bubble drop-on-demand ink jet printing
- Thermo-acoustic drop-on-demand ink jet printing
- Wet toner printing

Conductors can be used with one or more inks to achieve the combined electrical conductivity and luminous transmissivity required for a wide range of electro-optical devices and applications.

A hand-held display is one example of the application of above-described transparent conductors with certain limitations and properties.

In a hand-held display, the conducting line width is limited by the resolution of the printing method, which, in this example, is drop-on-demand ink jet printing with a feature limit of 50 microns. It is, therefore, not practical to define a pattern that includes an integral well within a continuous conductor. However, this does not mean that the metal reflow process cannot be used. It merely implies that the manner in which it is used must be one which is applicable to the present example. A suitable process involves a metal with a low melting temperature, such as zinc, which is laser treated to create a reflowed amorphous continuous metallic conductor. Using the same laser shown in Figure 1 but with a different irradiation pattern as illustrated in Figure 7 (particularly due to the impact of lens technology with spatial light modulators), it is possible to create the transparent conducting windows 12 by selectively oxidising the amorphous metal 14 in an oxidising environment 16 using the laser or high power LED 5 to assist the metal conversion to conductive oxide 18 or cermet induced via a solid-state or semi-liquid-state reaction process. The resolution of the contact window 12 is determined by the diffraction limit of the laser-lens set-up and by the oxidation edge control, which provides an interface zone

that progressively converts the metal to oxide thereby providing a graded interface to promote excellent mechanical and electrical properties.

This process uses a single printing step and a single ink that comprises a metal particle which, when oxidised, becomes a highly transparent but electrically conducting material. Although zinc has been cited for this particular example, low melting temperature metal alloys such as solders can be considered when the resulting oxidised window exhibits cermet-like properties when the metal oxide is not semiconducting.

Metal	Resistivity Ω-cm at "X"^{o}C	Conventional Melting Temperature ^{o}C
50 % Lead – 50 % Tin Solder	15.0×10^{-6} at 20^{o}C	216
Magnesium Alloy AZ31B	9.0×10^{-6} at 0^{o}C	627

Certain alloys could comprise materials that are semiconducting and insulating in oxide form resulting in the transparent window exhibiting a conductivity that is defined by the ratio of the cermet-to-semiconducting concentrations.

These two examples show the potential flexibility of the transparent conductor when it is applied onto a substrate. It is also possible to apply the conductor directly onto a surface that itself forms part of a device. An example of this flexibility is the construction of a light-emitting polymer pixel that is switched using a silicon or organic-based field-effect transistor, where the light-emitting polymer pixel has an outer electrode that is required to be electrically conductive and transparent.

Two or more processes may be employed so as to achieve a desired transparent conductor feature. A hybrid process may be the combination of the use of drop-on-demand ink jet printing and digital off-set lithographic printing.

A flat panel display device is a further example of an application of a transparent conductor. In this case, the luminous transmissivity advantageously approaches 100 % and the electrical resistance approach zero. Obviously, these perfect conditions are not

possible due to practical limitations resulting from the as-deposited and annealed electrical resistivity and the luminous waveband absorption coefficient of the selected transparent conducting material. It is known that changes in the concentration of the carrier of the transparent conducting material influence transmissivity through stronger absorption resulting from the increased charge carriers. The charge mobility associated with the transparent conducting material is therefore the prime target for producing improvements as an increase in mobility does reduce electrical resistance but does not result in a loss in transmission in the visible waveband (400 to 700 nm).

An alternate approach to obtaining high transparency and low electrical resistance is to separate the electrical performance from the optical performance by virtue of combining two independent materials that offer the best for both properties. The same hybrid process as for the hand-held display may be used; that is, the hybridisation of offset lithographic and drop-on-demand ink jet printing, although other production methods are obviously possible, to produce the transparent conducting element desired.

In its simplest form, the offset lithographic printing process is used to deposit a tram line structure that is connected at both ends of the lines so as to create a rectangular structure that is electrically continuous and that has a spacing between the tram lines of between 10 microns (which is the current limit in the direction of print for digital off-set lithography) and several millimetres. Figure 8 shows an end-on view of a conductive channel with metal tracks 50 on substrate 10.

One example of this form of process creates spacing between the tram lines within the rectangular structure of 100 microns. The spacing between these rectangular structures is 10 microns, providing a printed feature pitch of 130 microns (or 195 tracks per inch). The offset lithographic process in this example uses a 3 micron thick electroless plated insulating seed layer that has a track width of 10 microns. The printed seed layer 26 is immersed in an electroless plating bath and between 0.1 and 1.0 micron thickness of copper metal 32 is plated onto the seed layer as shown in Figure 9. Figure 9a shows a view from above of the rectangular well, whereas Figure 9b shows an end view of the electroless plated metal walls and printed transparent conductor 30. The copper thickness

32 modifies the actual bus bar and tram line spacing by virtue of the fact that the electroless plating is deposited on all exposed surfaces of the seed layer, hence a 10 micron wide seeding layer track will increase to 12 micron and the adjoining transparent window width, located between the opaque metal tram lines, will be reduced to 98 microns for a 1 micron electroless plated copper thickness. The resulting electroless plated copper film possesses a transparent window bus bar resistance of about 800 Ohms for a window length of 20 cm.

The transparent conductor window, in high transmissivity form, possesses a resistance of the order of 200,000 Ohms with the combined structure exhibiting a resistance of about 415 Ohms.

A transparent conductor of low resistivity (for example, a resistivity equivalent to a magnetron sputtered thin film having a resistivity of 2×10^{-4} Ω-cm) and having an equivalent area to the tram line structure described above would have a resistance of about 33,000 Ohms, which is at least 79 times more resistive than materials used in the tram line structure above, and it would absorb much more visible waveband radiation.

Within the tram line rectangle (or "constraining channel"), an insulating or a conducting channel or a combination of both may be provided, within which is defined the transparent conducting element in discrete or continuous form. The transparent conductor element can be a single layer structure or it can be a multiple layer structure comprising one or more discrete or blended materials. The transparent conducting element defined within the constraining channel can be due to the deposition of one droplet of ink or multiple droplets of ink. The multiple droplets of ink can be of the same chemical composition or of different compositions and chemistries such that the resulting liquid layers can be immiscible or can become fully mixed before the structure solidifies. The first droplet or multiple droplets of the same chemical composition can be partially dried to form a gel or semi-solid state that can then be impregnated with a second droplet or multiple droplets of ink, thus acquiring the further chemical properties. Figure 10, for instance, shows a conductive well 52 with an optically matched polymer infill 54 under the transparent material layer 30, between the metal tracks 50, to planarise the structure.

Current OEM print heads can be used to dispense precise quantities of ink into the channel which defines the conductor without the need for high resolution placement or very small volumes of ink in each drop.

An example of a patterned transparent conductor follows.

Assuming a square of aluminosilicate glass has a surface area of 10 cm by 10 cm and a thickness of 700 microns, it is highly transparent over the visible waveband covering 400 nm to 800 nm and also highly resistive. Onto this surface is printed, using conventional or digital, plate or plateless, off-set lithography, a series of parallel lines that have the following properties:

a printed line height of 3 microns;
a printed line width of 15 microns;
a printedline spacing of 985 microns; and
a printed line pitch of 1,000 microns.

The printed line material bonds to glass (which may act as a substrate) and acts as a receptor surface for electroless copper plating 32.

The printed lines are coated selectively, that is, only the lines are coated, and not the surrounding area, with a copper film of thickness 100 nm that exhibits a moderate resistivity of 10^{-5} Ω-cm. The geometry of the structure implies a conductor width of 21.1 microns due to the plating process as described above, and a cross-sectional area of 2.11×10^{-8} cm^2. The resulting resistance of a single 10 cm long conductor is 2,370 Ohms, which equates to a sheet resistance of 1 Ohm per square.

Two conductors are spaced 1 mm apart and are connected at their ends to form a rectangular containment well. The electrical connection nodes are such that the two separated conductors behave as a single conductor of double width and the same thickness. The connector (or link) resistance is effective over a connection length of 985 microns and a resistivity of 10^{-5} Ω-cm, providing a resistance of 46.7 Ohms and a sheet resistance of 1 Ohm per square. The link resistance is small in comparison with the long

conductors. The combined resistances of the connectors and the conductors give a total resistance of the rectangular well of 2390 Ohms or 23.9 Ohms per square (because of the change in aspect ratio between the connector and conductor). However, this assumes that the two conductors are separate whereas in fact they are connected. Consequently, the combined conductors will provide a sheet resistance of 1 Ohm per square because the resistance has halved but the area has doubled. It must be noted that the ratio of the resistivity to film thickness has remained constant even though the area of interest has changed.

Filling the rectangular containment well with a transparent conducting material that is electrically connected to the conductive walls of the well gives a sheet resistance which is the same as that calculated previously because the connectors bridging the two long conductors effectively short-circuit the material that is deposited between them. The aim of this structure is to ensure that charge generated in the centre of the well can reach the conductor and be carried away, the structure thereby acting as a continuous transparent conducting rectangular window.

It is known that thin film metal bus bars can be deposited onto a thin film transparent conductor to provide a means of removing charge as required above, for example, in a solar panel. The use of a bus bar is no different in design concept from the example above; it is only different in the manner in which it is produced and in its visibility to a user.

It is possible to isolate a rectangular well by removing the linking connections, thereby creating two conductors 20 spaced 985 microns apart, where the spacing is filled with a transparent conducting thin film 30. This is illustrated in, for example, Figure 11. In this case, if the two conductors 20 are connected to a multimeter or other form of resistance measurement, they will read a total resistance of 1 MΩ or so. If the length to width aspect ratio is 101:1, the resulting sheet resistance of this isolated well will be 9,900 Ohms per square.

It is also possible to create an interdigitated electrode structure as shown in Figure 12, which resembles two hair combs 70 with intermeshed teeth 72, which provides a structure that contains a large number of interconnected wells. The counter electrodes can be connected to the same potential as the corresponding electrodes or they can be connected to an alternative potential. This provides a means of removing charge from the transparent conducting window material, as required, for example, in solar cell applications.

The transmissive area is dictated by the ratio of the metal conductor to the space between conductors. In this example, the ratio of the space-to-metal introduces a transmission loss of order 1.5 %. This assumes that the instrument used to determine the total transmissivity can determine the influence of the metal conductors.

It is possible to measure the metal electrode that connects regions of the transparent conducting material. This electrode can have a very low sheet resistance, typically less than 1 Ohm per square. It is also possible to use a 4-point probe to measure the sheet resistance of the transparent conducting material deposited between the interdigitated electrodes. In this case, the sheet resistance is high, typically over 1,000 Ohms per square. The issue discussed below is whether these two statements are compatible with respect to the overall behaviour of a hybridised transparent conducting window.

Assuming that the interdigitated electrodes 70 of Figure 12 are at ground potential, in order for an induced charge to be able to sink to earth, it is necessary that the rate of dissipation of charge exceeds the rate of accumulation. This requires the understanding the dielectric relaxation time, τ_{dr}, which is a measure of the time it takes for a charge (electrons or ions) placed on a previously neutral material to relax to a uniform charge density in an isolated material or to leak to zero, if the material is connected to an electrical earth. The dielectric relaxation time, which is the product of the permittivity of free space, ε_o, the relative permittivity of the material, ε_r, and the resistivity of the material, ρ, is given by:

$$\tau_{dr} = \varepsilon_r \cdot \varepsilon_o \cdot \rho \qquad [1]$$

Assuming that the transparent conductor, which is located between the two metal conductors, which are themselves at earth potential, has a resistivity of 100 Ω-cm and a dielectric constant of 5, the resulting dielectric relaxation time, τ_{dr}, will be 4.42×10^{-11} seconds (44.2 pico seconds). This suggests that the charge should leak to earth very quickly; effectively instantaneously.

In order to determine whether the charge deposited on the material can move quickly enough for the desired application of the conductor, it is necessary to consider the mobility of the free charge, μ_{con}, where μ_{con} is the inverse of the product of free charge carrier density, n, electronic charge, q, and the material resistivity, ρ, and is defined as:

$$\mu_{con} = 1/nq\rho \qquad [2]$$

or, in terms of the dielectric relaxation time:

$$\mu_{con} = \varepsilon_o \varepsilon_r / nq\tau_{dr} \qquad [3]$$

From equation 3, for the dielectric relaxation time, τ_{dr}, to be low (that is, for relaxation to be quick), conduction mobility, μ_{con}, must be high. The density of free carriers can be increased to help this, but increasing the density of free carriers also influences the optical transmissivity negatively, and so it is more advantageous to increase the conduction mobility rather than the free charge carrier density.

The conduction mobility does provide a measure of the transit velocity from the charge dissipation source to the earth potential bus bar, because the material might not be of a form that possesses isotropic properties. This points to the fact that the manner in which nanoparticles contained in an ink droplet, ejected from a drop-on-demand ink jet print head come together on the receiving surface, is of significant importance in producing a high mobility device, as is the nature of any post-treatment (e.g., laser or rapid thermal annealing).

The transparent conducting material can take many forms, for example:

- Inorganic transparent conducting oxides [ATO, TO, ITO, FTO, ZnO, $SrCu_2O_2$, etc.]
- Organic [Pedot-PSS, Polyaniline, etc.]
- Organically modified ceramics [Metal alkoxides, etc.]

It has been shown by the example above that a transparent electrode may be produced that possesses very high optical transmissivity and electrical conductivity by combining printing processes. This combination produces a thin, highly conductive line that forms one wall of a constraining trench, the line not being visible at the standard viewing distance associated with laptops, mobile phones, hand-held personal processors and electronic games. The combination also gives a transparent conducting material constrained within the trench, that not only provides the electrical charge mobility, but also very high optical transmissivity across the luminous waveband.

Another method of making patterned or whole area (discussed below) transparent conductors involves surface etching and drop-on-demand ink jet printing as a further hybrid processing method.

It is known that screen printed metal tracks can be printed onto a transparent conductor to provide a means of providing an electric current to the transparent conductor, making use of a low resistance electrical bus bar/conductor that is not transparent. For display devices, it is necessary that such a bus bar is not directly observed by a user, since this would detract from easy viewing of the information displayed on such a device, which means limiting the bus bar width to about 30-50 microns, depending on the viewing distance and the actual resolving power of the user's eye. It is known that screen printing cannot produce a feature width of smaller than about 50 microns without considerable effort and particularly over large surface areas.

It is known that digital offset transfer plate/plateless lithographic, Gravure offset, and soft contact lithographic printing can produce very small features, in some cases much less

than 10 microns. This provides a means of generating a transparent conducting device that is based on a low resistance conductor, that is opaque and that is in contact with a continuous stripe or an array of transparent conductor windows which themselves possess low conductivity but which exhibit very high transmissivity in the visible waveband. The two adjoining materials can be independently modified so as to provide an optimised low resistance bus bar and high transparency conductive window performance independent of each other. This means that a transparent conducting element can be tailored to suit a given device type.

Methods that can be used to produce the constraining channel include:

- Continuous ink jet printing
- Drop-on-demand ink jet printing
- Ion beam etching
- Laser ablation
- Laser direct write deposition
- Lithographic printing
- Offset lithographic printing
- Offset stamping
- Patterned substrate (foils, sheets, paper) laminates
- Plasma reactive ion etching
- Screen printing
- Soft contact lithography
- Stencilling
- Surface dewetting
- Wet etching

Figure 13 shows a stripe structure comprising a metallic conductor (MC) 20 and a transparent conductor (TC) 30 deposited on a substrate medium 10 and electrically connected such that the metallic conductor 20 serves as a low resistance electrical highway providing electronic charge to be fed into the adjoining transparent conducting element 30 via the overlapping connection zone 40.

As shown in Figure 6, the metallic conductor 20 can be formed as a nanoparticle 22 or microparticle (24 of Figure 2a) structure that can be opaque or translucent and can be in the form of a connected particulate or a laser annealed form that includes amorphous, microcrystalline, polycrystalline, and single crystal dependent upon the film-substrate-processing scheme employed.

It is possible to use a modification of the patterned transparent conductor described above to provide a low cost means of producing a material that exhibits very high optical transmissivity with low electrical sheet resistance. The following examples can again use a 10 cm by 10 cm plate of glass, or a sheet of plastic such as PET or any other optically transmissive material. Examples of the basic process which will be further described below are:

1. Embedded + Coated
2. Integrated planar

All versions of the process make use of the same essential feature, which is the inclusion of an array of conductive bus bars that are not detectable by eye that sweep charge into or out of the whole area transparent conducting material that covers, and electrically connects to, the bus bar array.

For whole area structures, the bus bars can be defined as orthogonal sets of electrodes so that any size of panel can be cut from a larger sheet without impairing the overall electrical performance whilst still supplying an array of bus bar contacts along the edges of the diced plate.

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1. Embedded + Coated

As shown in Figure 14, a glass plate 80 can be coated with a self-assembled monolayer (SAM) 82 that provides a highly non-wetting surface. A laser is scanned over the plate surface to define a series of grooves 84 in the near surface and plate surface, the grooves

being below the detection limit of the eye and forming a set of containment trenches. The grooves, which can be produced using other methods, can be all in one direction (x or y) or in orthogonal directions (x and y), where the cross-over points provide connectivity between the both axes. The resulting grooves are filled with fluid 86 which can be achieved using precision spraying or drop-on-demand ink jet printing, where the wetting nature of the groove wall causes the ink to flow into the etched trench, leaving the surface free of ink because of the differential nature of the surface energy in the groove and that of the non-wetting SAM coating on the exposed surface between the grooves. The resulting solidified metal in-fill does not completely fill the groove so that the transparent conducting coating 88 can also flow into the groove and provide a direct electrical connection to the metallic bus bar. The SAM layer is easily removed using atmospheric ozone or UV lamp exposure, which chemically etches the monolayer in a manner similar to the photoresist residue removal approach associated with conventional semiconductor processing. The whole area transparent conducting coating can be applied using numerous methods, including:

- Doctor blading
- Drop-on-demand ink jet printing
- Electrostatic printing
- Electrostatic spraying
- Gel pressure lamination
- Pressure spraying
- Screen printing

The whole structure is then thermally annealed to effect good electrical connectivity and electrical performance between the two materials without impairing the very high optical quality. In this instance, the conductivity of the transparent coating is designed to provide good charge mobility but only over a limited distance; that is, to the nearest bus bar.

This embedded and coated whole area transparent conductor can be used in conjunction with a wide variety of substrate media, including crystalline silicon, dye-sensitised inorganic oxides, and organic/polymeric semiconducting for solar cell construction

2. Integrated Planar

An alternative approach to the preparation of the whole area transparent conductor is to use the hybrid printing method described above under the Patterned Transparent Conductors head, but using the ink jet printing process to deposit an optically transparent but electrically insulating material into the well, partially filling the deep well structure to the current limit of the digital off-set lithographic printing process employed to print the containment trench walls at a feature size below that detectable by eye. The in-fill material can be used to provide optical matching to the substrate media in order to minimise reflection losses. Once this filling has been completely dried, the whole area coating of the transparent conducting material can be completed in a manner similar to that described above. The completed substrate includes integrated metal bus bars and an encapsulating transparent conducting coating set on optical clear insulator, the insulator partly filling the containment trenches, and is thermally processed to provide the necessary performance and to promote thermal stability.

The printed containment well depth in the above examples is limited by the thickness of the printed seed layer, which is of the order of 2 microns for the off-set lithographic printing process. However, this layer thickness may be reduced with alternative processes, such as soft contact stamping, which could provide a seed layer thickness significantly less than 1 micron. Soft contact stamping has been shown to produce sub-micron scale features of nanometre thickness from a variety of polymeric materials over an area of about 30 cm by 30 cm, so much larger areas need to be patterned in a step-and-repeat process.

A further approach to manufacturing the whole area transparent conductor is to coat the whole surface area of the substrate media with the seed material and to use a laser ablation process to selectively remove the seed material thereby producing the required shallow groove in a material, which can then be electrolytically plated to provide the high conductivity copper bus bar structure whilst still retaining a very high open area that is devoid of any seed material or plated copper.

For some applications of the transparent conductor, it is not possible to use the processes described above. There are alternatives, however, which are described below and include:

1. in-line striped transparent conductor,
2. multilayer transparent conductor, and
3. mixed ink transparent conductor.

1. In-line Striped Transparent Conductor

It is possible to print a transparent conductor using a basic nanoparticle transparent conducting oxide based ink. The drop-on-demand ink jet printing feature resolution of 50 microns can be used for this process, the ink typically containing a solid content of ATO or ITO nanoparticles in the range 0.1% to 15% by volume. For the specific case of a 3% by volume solid containing ink, the resulting solidified transparent conductor ink, for a 200 micron wide transparent line electrode, has a thickness of order 200 nm. Given an electrical resistivity for the transparent conducting oxide film, after thermal annealing, of 10^{-3} Ohm-cm, the resulting sheet resistance will be of the order of 50 Ohms per square, with an associated transparency exceeding 90% at 550 nm. The individual pixels covered by the addressing line transparent conductor have a width of, for example, 200 microns on a pitch of 250 microns. The resulting line resistance for a 10 cm long transparent is 20,000 Ohms. Given the geometry of an individual pixel cell it is possible to replace the transparent conducting oxide between the pixels with a conducting link, for example one based on silver nanoparticles. In this case, the series resistance is reduced by 19% due to the higher conductivity nature of the links. As a result, the total resistance of the 10 cm long transparent electrode reduces to 16,200 Ohms.

2. Multilayer Transparent Conductor

If the luminous transmissivity can reduced, it is possible to construct a trilayer (though it could be binary or higher) transparent electrode using, for example, drop-on-demand ink jet printing. The multiplayer transparent electrode will comprise the following layer sequences as shown in:

- TCO/Metal/TCO
- TCO/Metal/TCO/Metal/TCO

The same 10 cm long and 200 nm thick transparent conductors can be used as were cited in the in-line transparent conductor described above. The metal nanoparticles can be, for example, silver, and the particle size and packing produce an equivalent thickness to the transparent conducting oxide films, which is 200 nm. The resulting resistance of a three-layer transparent conducting oxide-only structure is of the order of 6,600 Ohms. The equivalent resistance of the trilayer vertically stacked structure is of order 900 Ohms. The resulting transparent electrode resistance values calculated do not take into account any synergistic effects that might occur during annealing/sintering and that might promote a highly conducting band thickness greater than that actually due to the printed metal thickness. The transparent conducting oxide and metal nanoparticle film thickness can be adjusted so as to achieve a desired transmissivity-conductivity factor and that the number of layers comprising a transparent electrode can be selected to achieve an overall electrode resistance and luminous transmissivity.

The transparent conducting oxide portion of the multilayer can be continuous, whereas the metal layer portion of the multilayer can be deposited in a selective fashion so as to promote the equivalent of higher conductivity links within a continuous sea of transparent conducting oxide, while permitting the actual pixel areas to remain higher in luminous transmissivity.

3. Mixed Ink Transparent Conductor

This process makes use of a printing process that deposits a liquid film containing a mixture of nanoparticle inorganic transparent conducting oxide (i.e., TO, ITO, ATO, ZnO, etc.) and nanoparticle metal (i.e., Ag, Au, Cu, Al, etc.). The mixed ink enables the printing of whole area and patterned transparent conductors that exhibit a sheet resistance of less than 800 Ohms per square with a transparency of at least 85% at 550 nm wavelength (which is central to the luminous waveband). In order to achieve this in a

single ink, a highly conductive particle can be combined with a transparent conducting particle to introduce a small number of conduction centres in a p-type semiconducting sea.

A pure Ag nanoparticle film would possess a low luminous transmissivity due to the light absorbing nature of the silver. However, a random low concentration of metal nanoparticles dispersed within the, for example, transparent conducting oxide (TCO) coating will provide a means of enhancing charge injection shared between several nearest neighbour particles.

The ratio of the metal particle size to the transparent conductor particle size is an important factor in optimising the electrical and optical performance of the mixed particle film. As shown in Figure 17, assuming the particles are spheres, this is because equal sized particles will take up a larger volume for the same number of interparticle connections. Smaller particles that would achieve the same contact density, albeit at a slightly reduced contact area due to radius of curvature of the particles and taking into consideration the relative effects of surface roughness. It can be seen that ordered spheres can be closely-packed in either face-centred cubic or hexagonal structures, depending on the manner in which subsequent spheres are placed on top of the previously deposited sphere. For a two-sphere system of equivalent size, the packing argument remains the same, ignoring chemical considerations at this time. However, if the two spherical particles are of different size, then a structure such as that observed with the solid ball model of the NaCl lattice, namely a face-centred cubic structure, can be envisaged, which provides a minimum volume for a maximum nearest neighbour contact density (6 nearest neighbours) for each particle type. It is possible to construct this packing structure in a manner that permits metal-to-transparent conductor particle contact with or without transparent conductor-to-transparent conductor contact.

In order to achieve the maximum charge transfer, it is necessary to select a metal particle that is small enough to reside interstitially between the close-packed transparent conductor particles whilst still contacting each and permitting the transparent conductors to touch each other. Clearly, perfect packing of the particles is an idealised notion, but

from a practical standpoint, it does provide a means of combining metal and transparent conductor particles in such a manner that maximum conductivity and transmissivity can be achieved in a single coating that would not be achieved from a coating containing only one particle type.

Assuming that each particle is spherical and of the same diameter, it would be expected that one metal particle would contact 4 TCO particles. This suggests that, for a 3 % solution of ATO, 0.6% of the ATO can be substituted by Ag nanoparticles, thereby producing a 2.4% ATO/0.6% Ag/Aqueous/Surfactant ink. Assuming all of the Ag nanoparticles promote an increase in luminous absorption, it is anticipated that the transmissivity of about 94 % would reduce to a value of the order of 70%. However, given the multiple particle stacking nature of the thin film, some of the Ag particles will be aligned directly above other Ag particles, thereby reducing the effective absorption due to a reduce absorption capture cross-section, suggesting that the effective luminous transmissivity could be as high as 88 %.

If the metal particle were of a size that permitted contact between transparent conductor nearest neighbours and the associated metal particle, the volume of metal would be reduced over that area for identical particle size and the effect of direct absorption of light would be reduced in the ratio of the volumes. Clearly there is a specific relationship between the size of the metal particle and the transparent conductor on purely geometrical grounds if all surfaces are to touch, which from geometrical and mathematical considerations suggests that the metal particle diameter (assuming a spherical particle) must be of the order of 0.42 times the diameter of the transparent conductor. This suggests that a transparent conducting particle with a 18 nm diameter should be combined with a metal particle with a 7.56 nm diameter.

Binary nanoparticles systems behave differently from tertiary nanoparticle systems because of the relative potential interlocking behaviour of the particles, hence, the need for specific surfactants to assist particle flow and thereby reduced colloid/slurry viscosity.

Notwithstanding the fact that many nanoparticles are not spherical, a similar argument to that presented above still exists and as such, a metal particle dimension-to transparent conducting particle dimension ratio in the range of 0.415 to 0.435:1 (TCO particle) is envisaged.

In this example, the ink contains a distribution of both metal and transparent conducting oxide particles that, if not filtered, affects the manner in which such particle packing is achieved. Notwithstanding this, the metal particle-transparent conductor particle mix provides a benefit over a purely transparent conductor particle coating based on equivalent transparent conductor material.

The variable size of the metal and transparent conducting nanoparticles as described above assumes that the charge mobility within the transparent conducting particle is high and the intrinsic defects do not significantly limit the transport of charge carriers because the smaller metal particles will not actually be touching each other, and as such, do not create a direct conduction path for charge transport within the transparent conductor.

If the charge transport is limited by the defective nature of the transparent conducting nanoparticles, an alternate approach is to ensure that the metal particles touch each other at the same time as they touch their nearest neighbour transparent conductor particles. In this instance the dimensions of the metal and transparent conducting particles has to be the same in order to produce a close packing hexagonal structure that permits the necessary particle interconnection. In this case, the volume of metal will be increased over the two size particle ink described above with a concomitant impact on the optical transmissivity.

Given the difference in the conductivity nature of the semiconducting and metallic nanoparticles, it is essential that the stability of the Ag-ATO nanoparticle co-ingredients, to be stabilised in the same solution, be addressed so as to achieve optimum particle packing and in the ideal case, in a self-aligned manner.

It is also possible to use two independent printheads placed back-to-back or combined in a suitable locating jig such that droplets ejected from each printhead are co-incident at the constrained well centre to be filled or the surface area to be coated (within the limits of the accuracy of droplet ejection cone angle and printhead-to-substrate surface spacing). Given that for some printheads, it is possible to use a grey scale (for example, a scale with 8 levels, though other levels of processing are possible) approach to modify, in a digital manner, the total volume of ink that constitutes the equivalent of a single large volume drop, it is anticipated that subtle changes in nanoparticle mixing can be achieved at a local level. This means that the properties of adjacent segments of the same electrical conductor can be modified so as to achieve local changes in electrical conductivity, optical transmissivity and thickness.

Clearly, the concept described above can be applied to the generation of a tertiary, quaternary or higher order mixed nanoparticle transparent conducting element including the creation of inorganic-organic mixes and nanoparticle-polymer mixes by adjusting the number of printheads used and redesigning the multiple printhead jig if co-incident printing or precision back-to-back printing is required. Using the method of mixing nanoparticles to influence the electronic behaviour of the resultant thin film structure before and after annealing, it is possible to anticipate the deposition of a patterned transparent conductor that is based on p-type or n-type material, which can be used to produce transparent anodes and cathodes for applications including all-transparent (see through) displays and top transparent contacts for a wide variety of flat panel displays including silicon integrated micro devices.

The mixed transparent conductor can be tailored to provide suitable contact properties that affect the contact resistance, electronic barrier height, and charge transfer efficiency between the transparent conductor and the material with which it is in contact. It is anticipated that this can be achieved either by modifying the specific ratios of the nanopowders that comprise the thin film contact or by dispersing one or more nanopowders in a suitably conductive material such as a doped or intrinsically conducting polymer (e.g., polyaniline, Pedot-PSS) or a chemically derived conductive glass (e.g., sol-gel tin oxide). It is expected that the inclusion of such nanoparticles in, for example, the

conducting polymer film will assists the control of the electronic charge transfer between the transparent contact and the media to be contacted, especially conjugated or oligomeric semiconductors due to electronegativity modification and charge injection barrier reduction brought about by the concentration and nature of the nanoparticle, and will, to some degree, minimise the field-assisted transport of oxygen ions from the inorganic transparent conducting oxide particles into the material being contacted. The minimisation of oxygen ion migration to the contact-material interface will also suppress interfacial charge trapping effects that are known to cause dipole losses when reacting with hydrogen to form OH^- ions. In this context, it is possible to provide a multilayer structure using both material types based on separate ink supplies and/or drop-on-demand ink jet printheads in order to produce abrupt and diffuse interfaced structures that provide a transparent contact on oxygen-sensitive materials.

The production of both n- and p-type conducting transparent electrodes opens up the possibility of creating p-n junctions based on the printing of p-type and n-type materials that can be achieved either as conventional vertical stacked structures or as a single layers comprising a homogeneous distribution of n- and p-type material in close proximity to create novel electronic structures.

In order to produce a transparent conducting electrode possessing the lowest resistance, it is necessary to optimise the charge mobility within a nanoparticle and the charge transfer across the inter-particle contact surface area. In this respect, this contact interface exhibits a low contact resistance and charge transfer by virtue of matching the electronic band offsets of the two materials. The choice of material, for example, for a mixed metal-oxide nanoparticle ink, must exhibit a low electronic charge barrier which can be determined using band-offset calculations. For particle-based coatings, it can be important that the contacting surface area is made as large as possible to minimise interfacial contact resistance, which in the case of a coating comprising transparent conducting particles dispersed in a conducting binder, can be achieved by ensuring that the choice of conducting binder readily wets the nanoparticles and when in contact provides the best electronic conduction band alignment.

Suitably coated transparent conducting particles can be produced using the selective withdrawal technique. This provides means for coating individual particles with an electronically matched material and the matched material can readily undergo reflow and coalescence with nearest neighbour particles when heated so as to produce a larger contact area that is controlled by surface tension and surface wetting. The resulting inter-particle plug will then provide means for minimising charge transfer throughout the transparent conductor.

The mixed nanoparticle ink can include optical micro and sub-micro spheres that are optically clear such as would be the case with silica or polyethylene structures. The micro spheres, which can be conducting, semiconducting, or insulating, enhance luminous transmissivity and also influence the geometrical dispersion of the emitted light, as well as promoting improved durability and wear resistance. The nano- or microspheres can be added to a printed transparent conductor before it has been dried so that the spheres are retained in the material as shown in Figure 15. The nano- or microspheres can be added to a surface to provide a distribution of dried spheres 24 that is then embedded by printing a second transparent conductor ink 96, such as a metal alkoxide sol or intrinsically conducting polymer, that coats around the spheres to provide mechanical binding and electrical transport. Figure 15 shows a transparent or opaque substrate 90 with a first ink containing a transparent bonding layer 22; a second ink containing insulating or conducting microspheres 24 which bond to the first layer as it dries; and a third ink containing a transparent conductor layer 96. Figure 16 shows the microspheres 24 embedded in a transparent conducting layer 98.

The mixed nanoparticle ink can include dyes and pigments that provide transmissive, reflective, and luminescent colouration.

A number of applications, such as electrochemical or electro-optical sensors can require a transparent electrode that permits a gas or a liquid to pass through it and penetrate into the underlying material where it undergoes a chemical reaction that is assisted by the electric field provided by the transparent electrode in conjunction with a counter-electrode. Porous electrodes may be made by several methods, including:

- Controlled surface wetting through a laser etched non-wetting SAM monolayer or deposited coating
- Controlled surface wetting through ink additives
- Controlled surface wetting through photolithographic patterning of a non-wetting SAM monolayer
- Controlled surface wetting through selective area electrostatically-induced electrical potential
- Controlled surface wetting through self-assembled monolayer patterning
- Molecular scale pattern templating
- Nanoparticle aerogelation
- Nanoparticle self-organisation

In the case of the molecular scale pattern template, an ink containing a very low concentration, in the range 0.001% to 5%, of a self-assembling polymer is first deposited and dried to provide a suitable interconnection pattern. A second ink containing the specified transparent conducting materials that is chemically compatible with the template monolayer is then applied using, for example, drop-on-demand ink-jet printing. The transparent conductor ink decorates the monolayer template pattern in those areas that expose the underlying substrate surface. The complete structure is then exposed to a chemical environment, such as Faraday cage oxygen plasma, which provides a means of removing the monolayer template pattern without damaging the surface that is exposed when the template material is removed. The resulting porous transparent conductor can be left in the as-deposited state or can undergo rapid thermal or pulsed laser processing to enhance the transparent conductor performance, providing allowance is made for the potential damage that might accrue to the underlying material in contact with the porous transparent electrode.

Additives, such as specialist surfactants and surface structure alignable liquid crystals, can be included in the transparent conductor ink design. These additives can promote nanoparticle or in-situ chemical reaction self-organisation. The characteristics of such

self-organisation dictate the extent to which the porosity is maintained at the nano- or micro-scale.

The composition of the transparent conductor ink can be so modified so as to promote spontaneous localised dewetting due to the nature of the ink viscosity and surface tension, and the substrate surface energy, which can induce differential wetting behaviour via the Marangoni effect promoting or resisting natural wetting behaviour. In this respect, mixed solvent inks are known to affect the wetting of surfaces and, in some cases, to promote controlled patterning of surfaces from an array of discrete dots to interconnected spinoidal dewetting and dendritic patterning.

A self-assembled non-wetting monolayer can be used, deposited, for example, using drop-on-demand ink jet printing, the monolayer being patterned in a step-and-repeat manner using an integrated UV Lamp patterning or Laser digital pattern transfer to create wetting and non-wetting regions on the surface. A second transparent conductor ink is delivered to the surface using ink jet printing that segregates the wetting lands to produce the required transparent conductor layout, with the patterning-defining monolayer material being removed using chemical means.

Applications for transparent conducting structures other than transparent electrodes for flat panel display devices are possible.

Numerous applications have been conceived that benefit from the application of patterned transparent conducting thin films, including:

- 2- and 3-dimensional periodic structures
- ~~Electrochromic "Smart" windows: [patterned and whole area]~~
- Electronic blinds and large area shutters
- Electro-optic micro shutters: [LCD, ferroelectric, electrochromic]
- Electro-optic switches: [organic and inorganic]
- Flat panel displays: [Low and high resolution, current and field switched active and passive addressing]

- Integrated optical devices: [modulators, detectors, spectrum analysers, converters, spatial light modulators]
- Light emitting diodes and lasers: [organic, polymeric, inorganic]
- Micro sensors: [discrete devices and arrays for gas sensing]
- Non-linear optical devices: [organic and inorganic active waveguides]
- Photovoltaic cells and switches: [organic and inorganic]
- Touch-sensitive switches: [capacitive]
- Transparent antennas
- Transparent heaters and ice demisters: [large area and integrated device micro heaters]
- Transparent micro heaters

There follow examples of the above in order to illustrate the diverse manufacturing potential of printed and directly patterned transparent conductors.

2- and 3-dimensional periodic structures

It is known that colloids have the ability to self-assemble into 2- and 3-dimensional periodic structures under specific conditions. Given control over the nanoparticulate size, dielectric constant, monodispersivity, refractive index, and the wavelength of the incident photons, it is possible to construct photonic band gap structures, including tunable band gap behaviour, that exhibit unique electromagnetic radiation diffraction gratings, routers, interconnectors, and switches. In this respect, mixed nanoparticles and hybridised nanoparticles in organic systems, including controllable orientation polymers and organic crystals, provide a means of expanding potential applications and performance diversity, particularly for applications covering all-optical integrated micro photonic circuits, all-optical computers, and all-optical telecommunications systems.

Touch-sensitive switches [capacitive]

A manufacturing method based on one or more of the ideas and concepts described in this document can be used to produce the transparent contact for a capacitive touch switch.

Photovoltaic cells and switches

A manufacturing method based on one or more of the ideas and concepts described in this document can be used to produce a transparent contact for a light dependent proximity switch for use on, for example, a control panel.

Transparent antennas

A manufacturing method based on one or more of the ideas and concepts described in this document can be used to produce a transparent antenna pattern and interconnection that can be used in, for example, automobile screens and on contactless radio-frequency smart cards, electronic money vouchers, security devices that include displayed media, and electronic passes.

Transparent heaters and ice demisters

A manufacturing method based on one or more of the ideas and concepts described in this document can be used to produce heated transparent screens and mirrors. A resistive transparent heater, as might be employed in the heating of aircraft windscreens, automobile windscreens, internal/external mirrors and lights coverings, formed in a spiral, straight line, or any other pattern can possess a wide range of resistance based on the electrical resistivity, length, width, and thickness selected for the transparent heating element. The terminations to the transparent heating element could be deliberately made metal-rich or graded up to pure metal by, for example, using a dual printing process to print the transparent conductor with one ink based on transparent conducting oxide nanoparticles and the metal connector pads with a second ink based on metal nanoparticles of chemically convertible solution.

Transparent micro heater

A transparent micro heater would be required to permit the heating of a chemical reagent in a lab-on-a-chip experiment where the reaction driven by the heating process needs to be continuously monitored using optical methods. The optical method can be achieved using end-butted optical waveguide transfer of transmitted light that is provided by a diametrically opposed complementary waveguide or light-emitting device that provides the means of illuminating the chemical reaction cell. The heating device could be a simple planar structure that heats the reaction cell from above or below; or it can be a planar

structure that heats the reaction cell radially since the heater configuration would form a containment well.

The resistance of an annular micro heater including the resistive legs that contact the annulus is given by:

$$R_{Heater} = \pi r \rho / 2wd \qquad [4]$$

or

$$R_{Heater} = (2\pi r - x)\rho / wd \qquad [5]$$

Where,

ρ	=	electrical resistivity of the transparent conducting film	[Ω-cm]
d	=	thickness of the transparent conducting film	[cm]
w	=	width of the annulus	[cm]
r	=	radius to the centre of the annulus	[cm]
x	=	spacing between contact electrodes from the same side	[cm]

The resistance of the annulus is determined by the transport path being around both halves of the annulus for electrodes that contact the circular heater from opposite sides (180^{o} apart). For example, a 100 micron diameter well is formed with a transparent conducting film annulus of width 50 microns and connecting legs of length 50 microns. The transparent conducting film has a thickness of 200 nm (0.2 microns) and exhibits a moderate electrical resistivity of 10^{-1} Ω-cm. The resulting micro heater resistance is 19,634 Ohms with a luminous transmissivity of more than 90 %.

CLAIMS

1. An electrical conductor having a region comprising transparent electrically conductive material having dispersed therein electrically conductive particles formed from material having a higher conductivity than the transparent material.

2. A conductor according to claim 1, wherein the transparency of that region of the conductor is greater than 70%, preferably greater than 80%, at 550 nm wavelength.

3. A conductor according to claim 1 or 2, wherein the conductive particles comprise nanoparticles.

4. A conductor according to any preceding claim, where the conductive particles are of uniform or non-uniform size, and have a mean size less than 1000 nm.

5. A conductor according to any preceding claim, where the conductive particles have a mean size less than 100 nm, preferably less than 20 nm.

6. A conductor according to any preceding claim, wherein the ratio of the size of the conductive particles to the size of particles of the transparent material is equal to or less than 1:1, preferably less than 0.5:1.

7. A conductor according to any preceding claim, wherein the transparent material is selected from the group consisting of a transparent conductive oxide and a transparent polymer.

8. A conductor according to any preceding claim, wherein the conductive particles comprise metal particles, preferably at least one of silver, gold, copper, aluminium, tin, zinc, lead, indium, molybdenum, nickel, platinum and rhodium particles.

9. A conductor according to any preceding claim, wherein the ratio of the number of particles of the transparent material to the number of conductive particles is substantially uniform throughout the conductor.

10. A conductor according to claim 9, wherein the ratio of the number of particles of transparent material to the number of conductive particles is equal to or greater than 4:1.

11. A conductor according to any of claims 1 to 8, wherein within the region the ratio of the number of particles of transparent material to the number of conductive particles is locally varied in order to provide sub-regions with different conductivity, optical transmissivity and/or thickness .

12. A conductor according to any preceding claim, wherein said region of the conductor has a sheet resistance of less than 800 Ω per square.

13. A conductor according to any preceding claim, said region comprising a single layer of transparent material having said conductive particles dispersed within.

14. A conductor according to any of claims 1 to 12, wherein, in said region, the conductive particles are located between respective layers of transparent material.

15. A conductor according to any preceding claim, said region further comprising translucent spheres embedded within the transparent material.

16. A conductor according to any preceding claim, comprising at least one conductive track providing a source or sink for electrical charge transport to and from said region.

17. A conductor according to any preceding claim, wherein said track is of lower transparency than said region at 550 nm wavelength.

18. A conductor according to claim 16 or 17, wherein the track has a width equal to or less than 100 microns.

19. A conductor according to claim 16 or 17, wherein the track has a width equal to less than 50 microns.

20. An electronic device comprising at least one electrical conductor according to any preceding claim.

21. A device according to claim 20, comprising a p-type transparent electrically conductive electrode and an n-type transparent electrically conductive electrode each comprising a conductor according to any of claims 1 to 17.

22. A method of fabricating an electrical device, comprising printing on a substrate an electrical conductor comprising transparent electrically conductive material having dispersed therein electrically conductive particles formed from material having a higher conductivity than the transparent material.

23. A method according to claim 22, wherein a fluid comprising both the electrically conductive particles and the transparent material is printed on the substrate.

24. A method according to claim 22, wherein a first fluid comprising the transparent material and a second fluid comprising the electrically conductive particles are printed on said substrate.

25. A method according to claim 24, wherein the fluids are printed using respective printheads.

26. A method according to claim 24 or 25, wherein the first and second fluids are printed sequentially.

27. A method according to any of claims 24 to 26, wherein electrically conductive particles are selectively printed so as to form regions of locally increased density and/or thickness on the substrate.

28. A method according to any of claims 24 to 27, wherein the transparent material is printed over previously printed electrically conductive particles.

29. A method according to any of claims 24 to 27, wherein the electrically conductive particles are printed over previously printed transparent material.

30. A method according to any of claims 24 to 28, wherein the electrically conductive particles are deposited directly on to the substrate.

31. A method according to claim 23 or 24, wherein the first and second fluids are printed simultaneously.

32. A method according to any of claims 22 to 31, wherein the printing of the transparent material and the electrically conductive particles forms a printed hybrid, the method further comprising annealing the printed hybrid.

33. The use, in the manufacture of an electrical conductor comprising transparent electrically conductive material, of metallic nanoparticles.

34. The use according to claim 33, where the nanoparticles are dispersed within the transparent material to improve conductivity thereof.

35. An electrical conductor comprising transparent spheres embedded within transparent electrically conductive material.

36. A conductor according to claim 35, wherein the spheres have a mean diameter of less than 10 microns.

37. A conductor according to claim 35 or 36, comprising, between the transparent electrically conductive material and a substrate, a layer of transparent material to which the spheres are secured.

38. A conductor according to claim 37, wherein the spheres and the layer of transparent material are substantially optically matched.

39. A conductor according to any of claims 35 to 38, wherein the transparent material is selected from the group consisting of a transparent conductive oxide and a transparent polymer.

40. A conductor according to any of claims 35 to 39, wherein the spheres are formed from one of conductive, semiconductive or insulating material.

41. A method of fabricating an electrical device, comprising printing on a substrate an electrical conductor comprising transparent electrically conductive material and transparent spheres.

42. A method according to claim 41, wherein a first fluid comprising the transparent material and a second fluid comprising the spheres are printed on said substrate.

43. A method according to claim 42, wherein the fluids are deposited using respective printheads.

44. A method according to claim 41 or 42, wherein the first and second fluids are deposited sequentially.

45. A method according to claim 44, wherein the transparent electrically conductive material is initially printed on to the substrate, and the spheres are subsequently deposited on the transparent material before complete drying thereof so that the spheres become embedded within the transparent material.

46. A method according to claim 44, wherein a second transparent material is initially deposited on to the substrate, the spheres being deposited on that transparent material before complete drying thereof so that the spheres are retained by that transparent material, the transparent electrically conductive material being subsequently deposited between the retained spheres.

47. A method according to claim 46, wherein the second transparent material is cured using electromagnetic radiation prior to the deposition of the transparent electrically conductive material.

48. A method according to any of claims 40 to 47, wherein the printing of the transparent material and spheres forms a printed hybrid, the method further comprising annealing the printed hybrid.

49. The use, in the manufacture of an electrical conductor comprising transparent electrically conductive material, of transparent spheres.

50. The use according to claim 49, where the spheres are embedded within the transparent material to improve the photon transmissivity of the conductor.

51. The use according to claim 49 or 50, where the spheres are embedded within the transparent material to improve durability and/or wear of the conductor.

52. An electrical conductor comprising transparent electrically conductive material and at least one conductive track formed from nanoparticles and providing a source or sink for electrical charge transport to and from the transparent material.

53. A conductor according to claim 52, where the nanoparticles are of uniform or non-uniform size, and have a mean size less than 1000 nm.

54. A conductor according to claim 52 or 53, where the nanoparticles have a mean size less than 100 nm, preferably less than 20 nm.

55. A conductor according to any of claims 52 to 54, wherein the transparent material is selected from the group consisting of a transparent conductive oxide and a transparent polymer.

56. A conductor according to any of claims 52 to 55, wherein the nanoparticles are metallic, preferably at least one of silver, gold, copper, aluminium, tin, zinc, lead, indium, molybdenum, nickel, platinum and rhodium nanoparticles.

57. A conductor according to any of claims 52 to 56, wherein the conductor has a transparency greater than 70%, preferably greater than 80%, at 550 nm wavelength.

58. A conductor according to any of claims 52 to 57, wherein the track and the transparent material partially overlap.

59. A conductor according to any of claims 52 to 58, comprising a plurality of conductive tracks at least partially surrounding the transparent material.

60. A conductor according to any of claims 52 to 59, wherein the track directly contacts the transparent material.

61. A conductor according to any of claims 52 to 59, comprising further, electrically conductive material disposed between the track and the transparent material.

62. A conductor according to any of claims 52 to 61 disposed on a transparent substrate.

63. A conductor according to claim 62, comprising further transparent material located between the substrate and the transparent electrically conductive material.

64. A conductor according to any of claims 52 to 63, wherein said track is of lower transparency than the transparent material at 550 nm wavelength.

65. A conductor according to any of claims 52 to 64, wherein the track has a width equal to or less than 50 microns.

66. A method of fabricating an electrical conductor, comprising selectively depositing on a substrate a fluid comprising electrically conductive particles, causing the deposited

particles to form at least one continuous, discrete conductive track, and forming at least one region of transparent electrically conductive material on said substrate, the track providing a source or sink for electrical charge transport to and from the transparent material.

67. A method according to claim 66, wherein the track is formed by at least one of sintering, melting and annealing.

68. A method according to claim 66 or 67, wherein the region of transparent material is formed by selectively printing said transparent material on said substrate, preferably using a drop on demand printing technique.

69. A method according to claim 68, wherein the transparent material is deposited over the conductive tracks.

70. A method according to claim 66 or 67, wherein the track is formed from electrically conductive material which, when oxidised, becomes at least partially transparent, the region of transparent material being formed by selectively oxidising portions of said track.

71. A method according to claim 70, wherein the region of transparent material is formed by ultra violet oxidisation.

72. A method according to any of claims 66 to 71, wherein the electrically conductive material comprises a metal with a lower melting temperature than that of the transparent material.

73. A method according to any of claims 66 to 72, wherein the track and the region of transparent material are formed using nanotechnics.

74. A method according to any of claims 66 to 73, wherein the fluid is selectively deposited using a drop on demand printing technique.

75. A method according to any of claims 66 to 74, wherein the fluid is deposited within grooves formed on the substrate, preferably so as to partially fill the grooves.

76. A method according to claim 75, wherein the grooves are formed in a coating formed on the substrate.

77. A method according to claim 75 or 76, wherein the grooves are formed by laser ablation.

78. A method according to any of claims 66 to 78, wherein the track is formed subsequent to the formation of the at least one region of transparent electrically conductive material on said substrate.

79. A method of fabricating an electrical conductor, comprising selectively forming on a substrate at least one conductive track defining a window at least partially surrounded by said track, and subsequently using the technique of drop-on-demand printing to deposit transparent electrically conductive material within said window, the track providing a source or sink for electrical charge transport to and from the transparent material.

80. A method according to claim 79, wherein the track is formed on the substrate using a lithographic printing technique.

81. A method according to claim 79, wherein the track is formed on the substrate using a plating technique.

82. A method according to any of claims 79 to 81, wherein the track provides a containment well for the transparent material.

83. A method according to any of claims 79 to 82, wherein a single layer of transparent material is deposited within said window.

84. A method according to any of claims 79 to 83, wherein a plurality of layers of transparent material are deposited within said window.

Abstract

Transparent electrical conductors comprising regions of high transparency and regions of lower transparency, but higher conductivity. This allows electrical connection through the conductor, while retaining its transparency for such applications as hand-held device display screens or transparent antennas, for example.

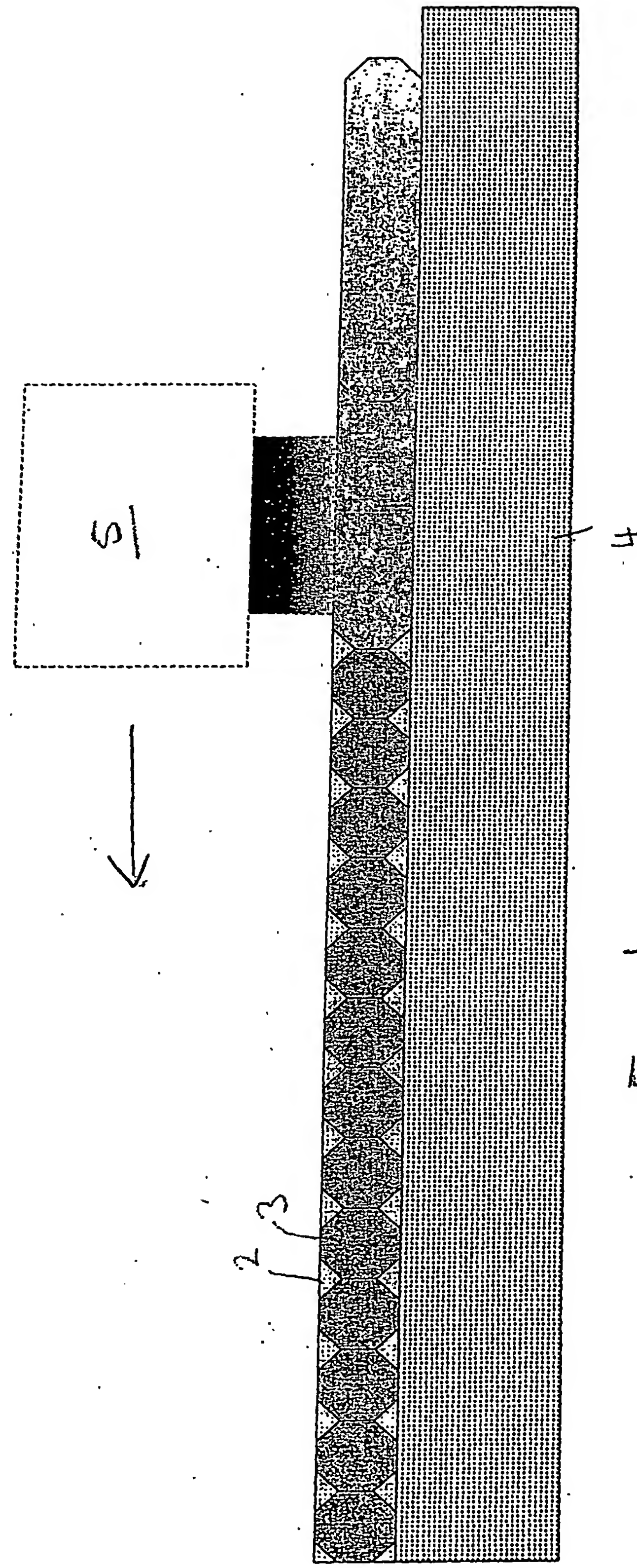

Fig 1

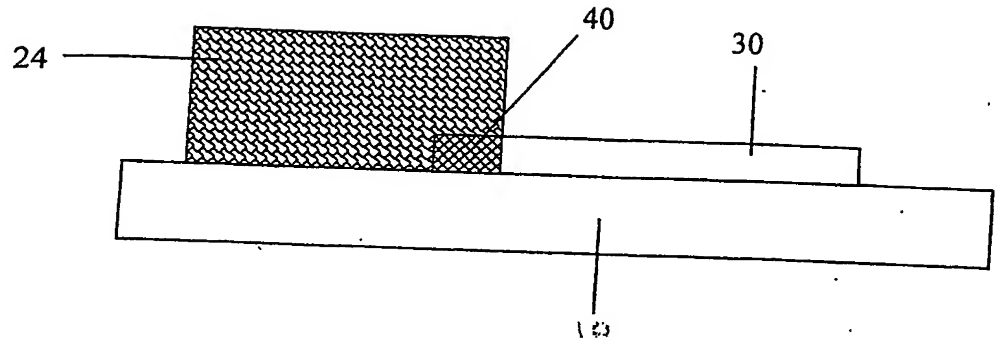

Fig 2a

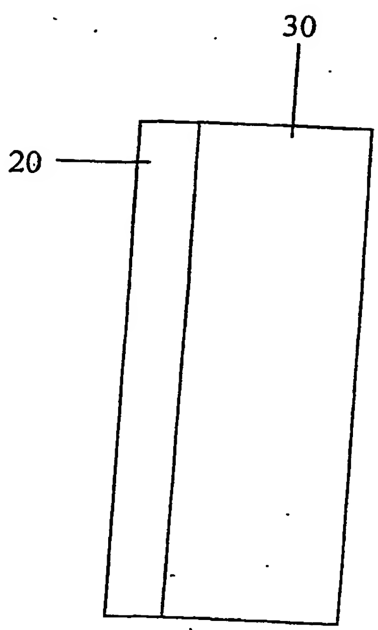

Figure 2b

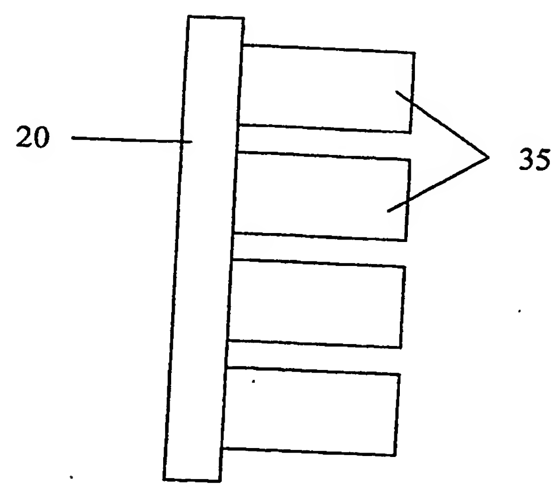

Figure 3

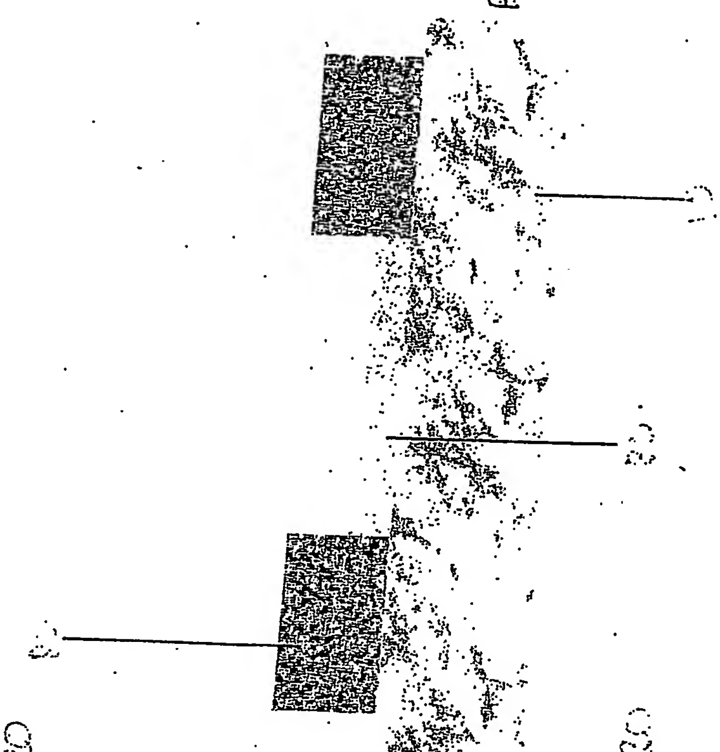

Fig 4b

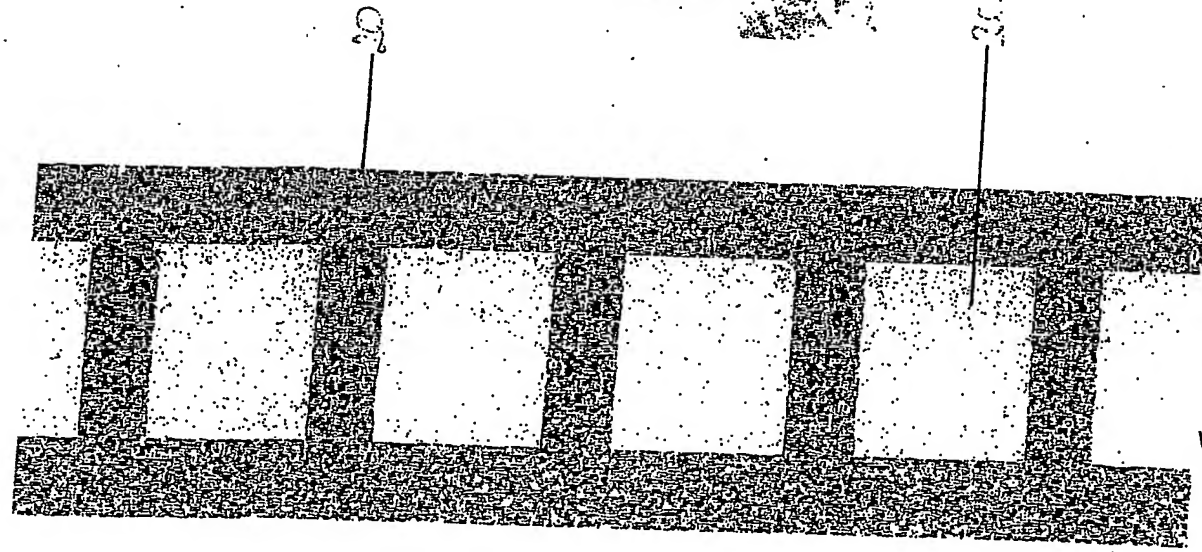

Fig 4a

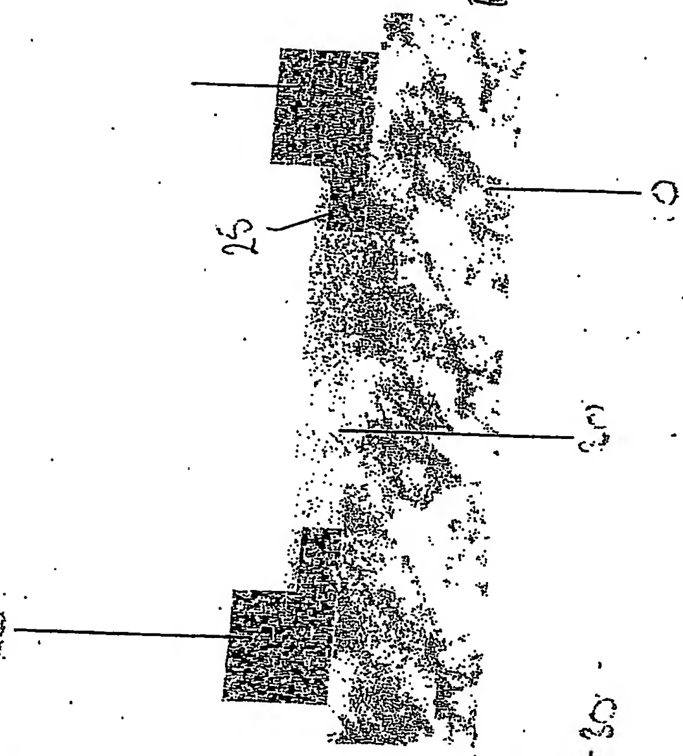

Fig 5b

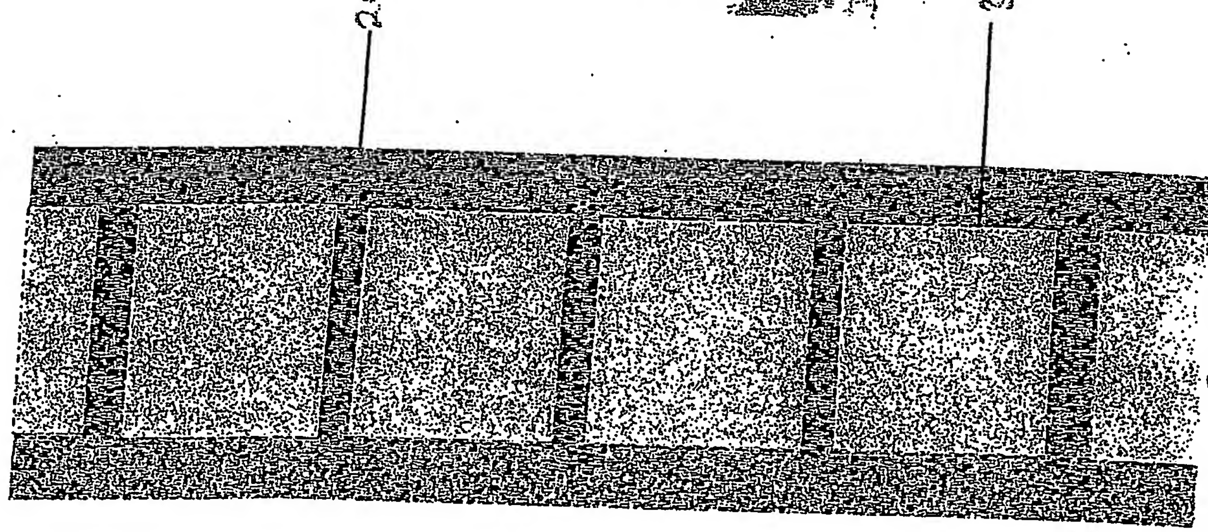

Fig 6a

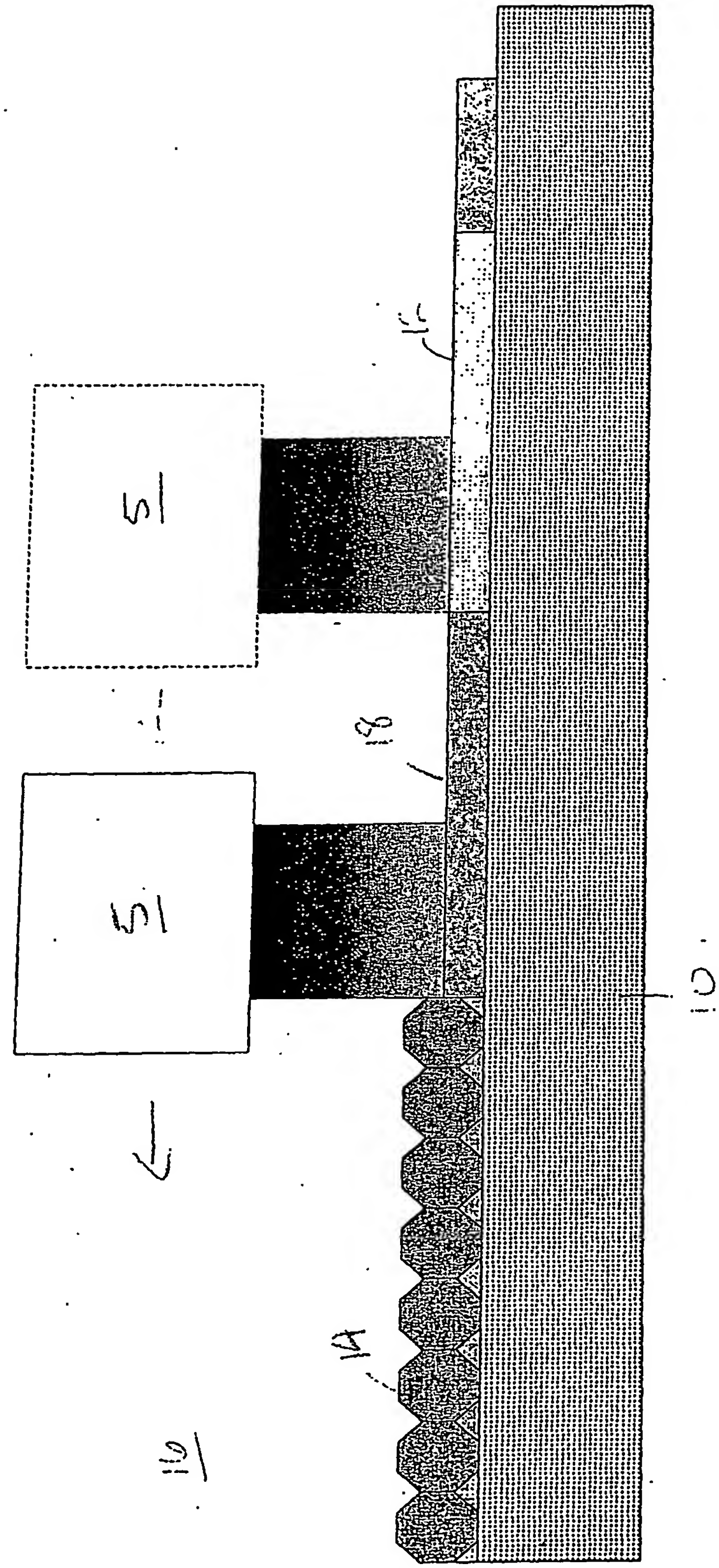

Fig. 7

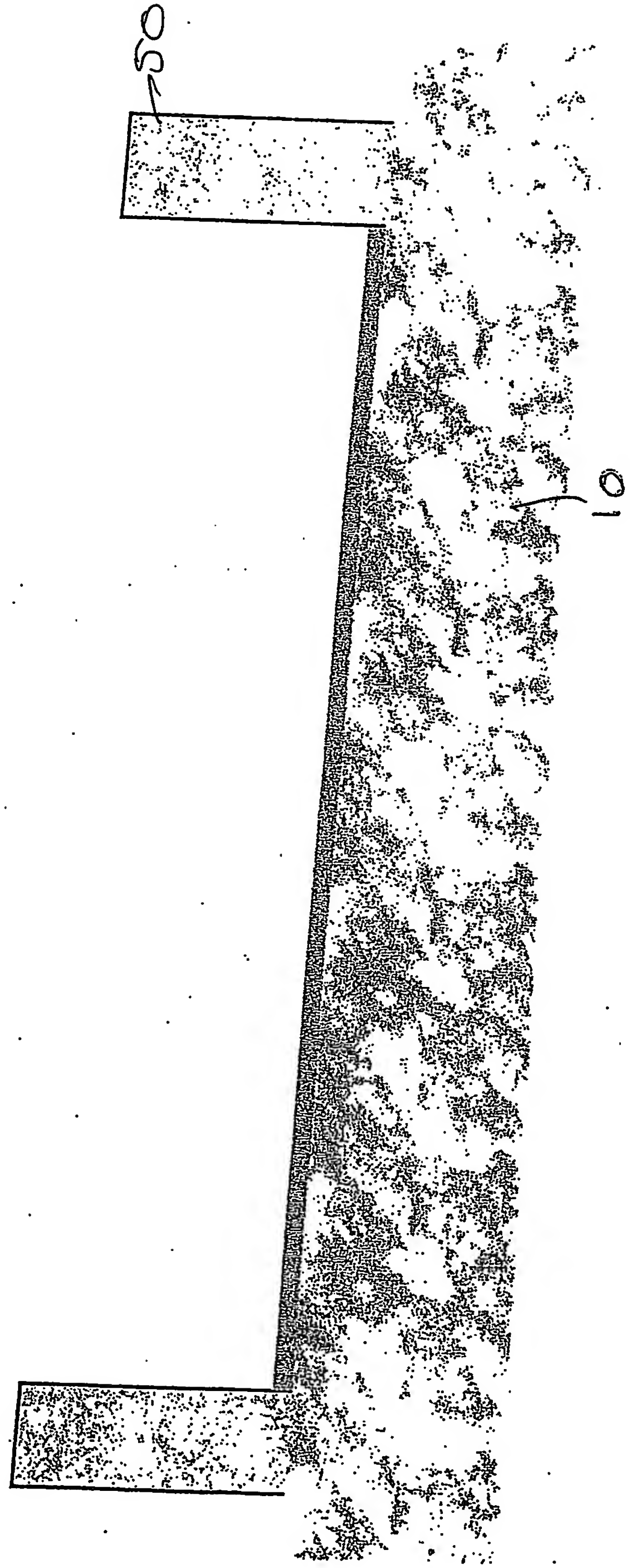

Fig 8

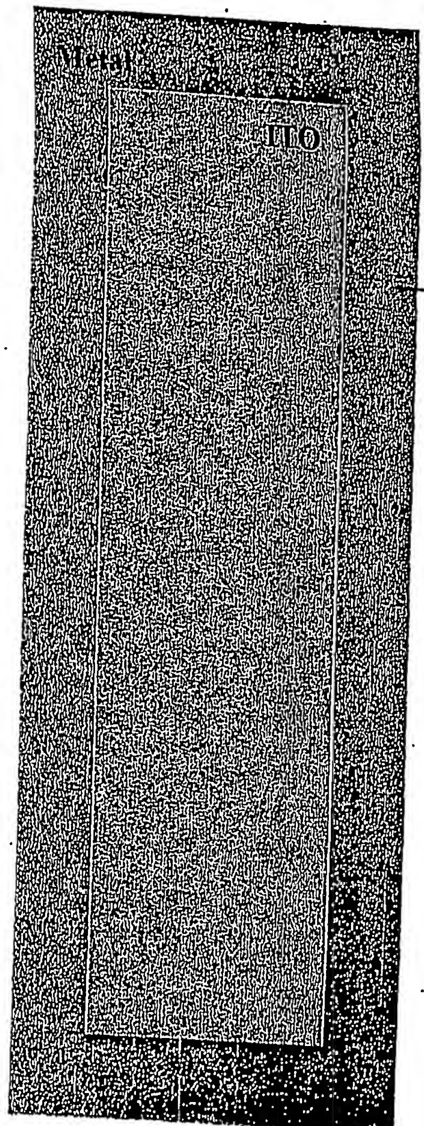

Fig 9a

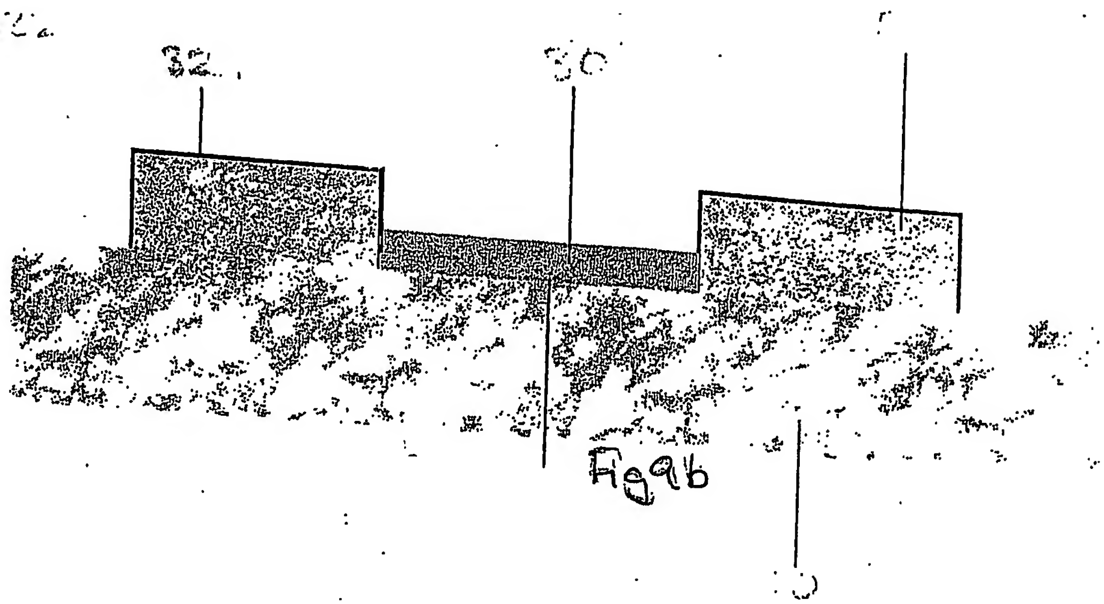

Fig 9b

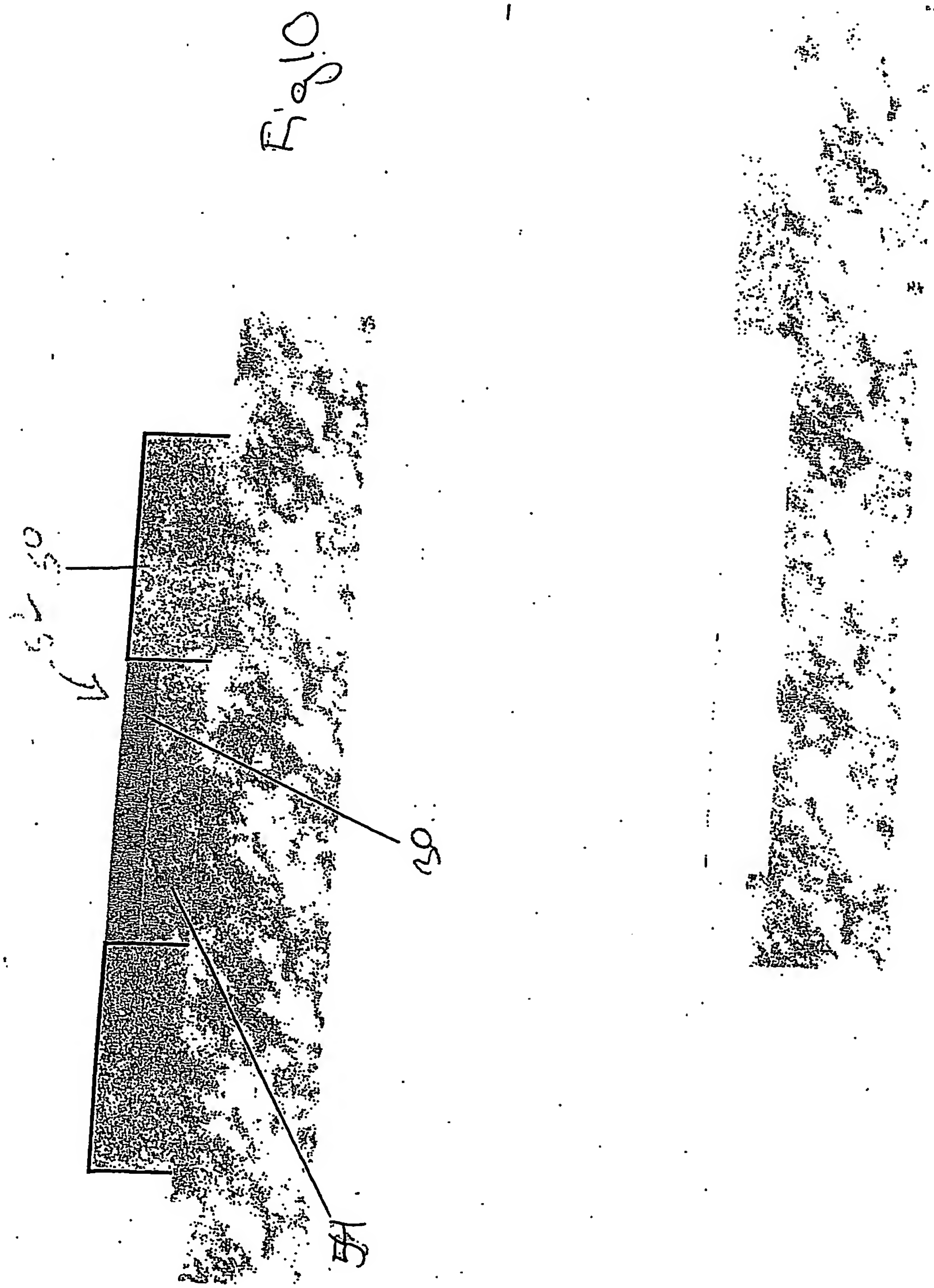

Fig 10

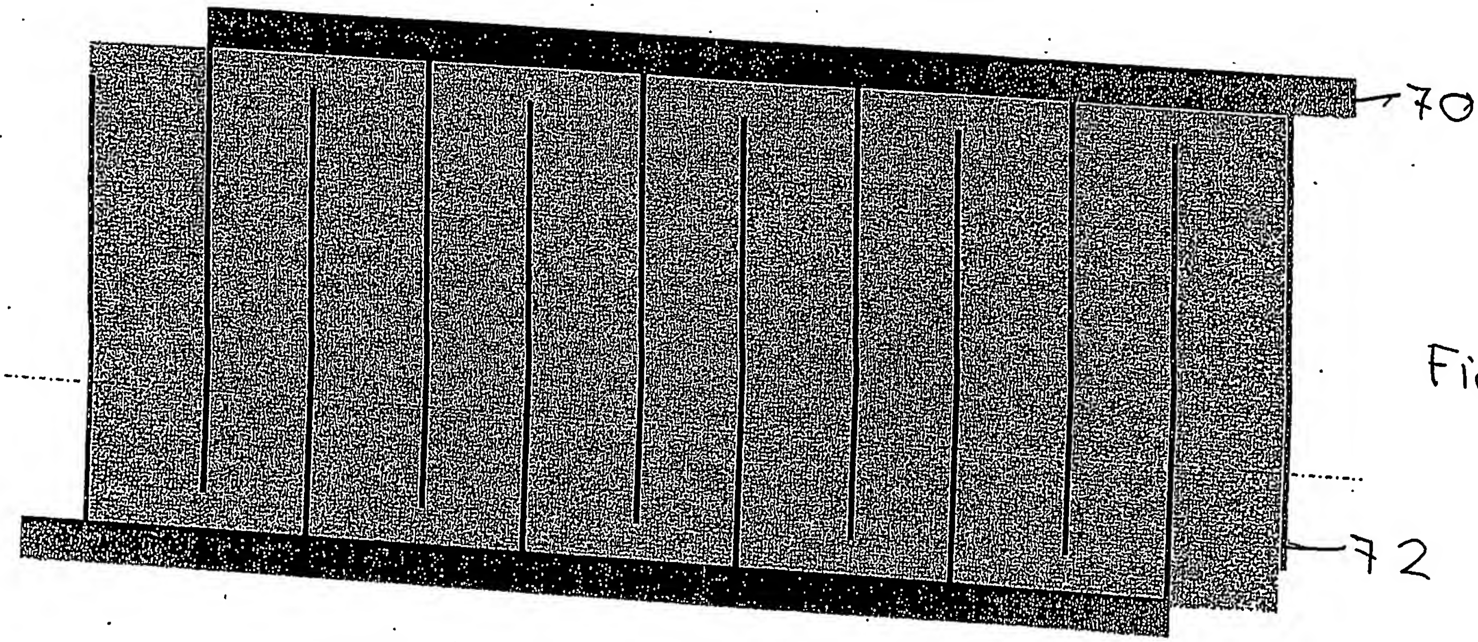

Fig 12a

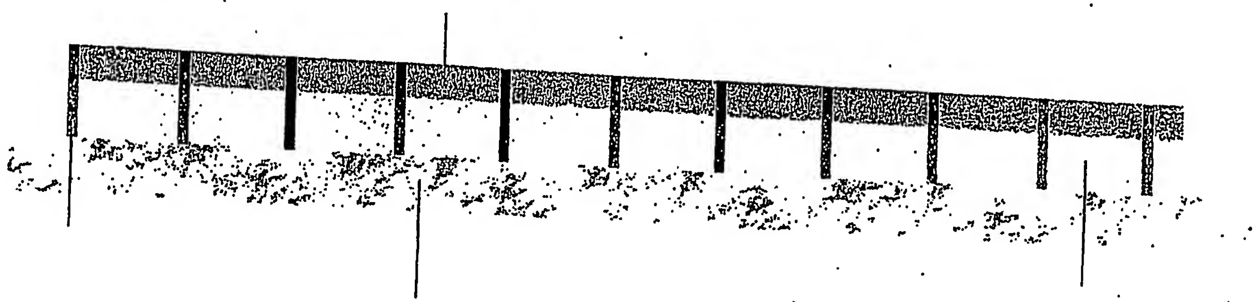

Fig 12b

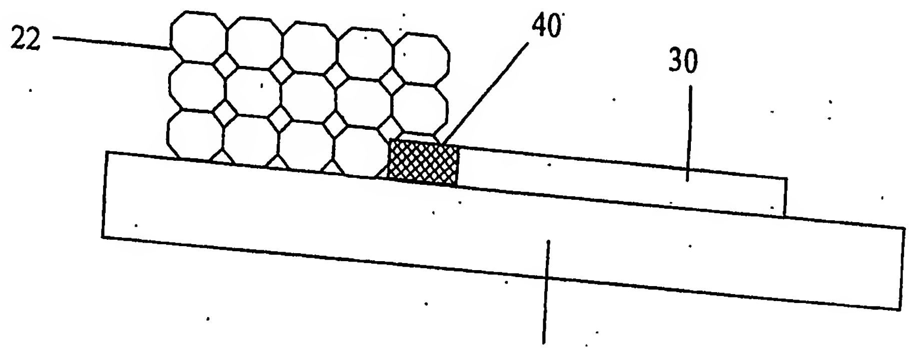

Fig. 6

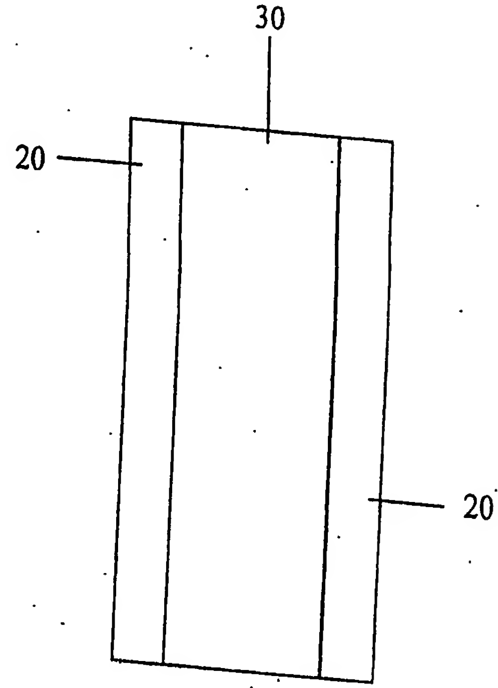

Figure 11

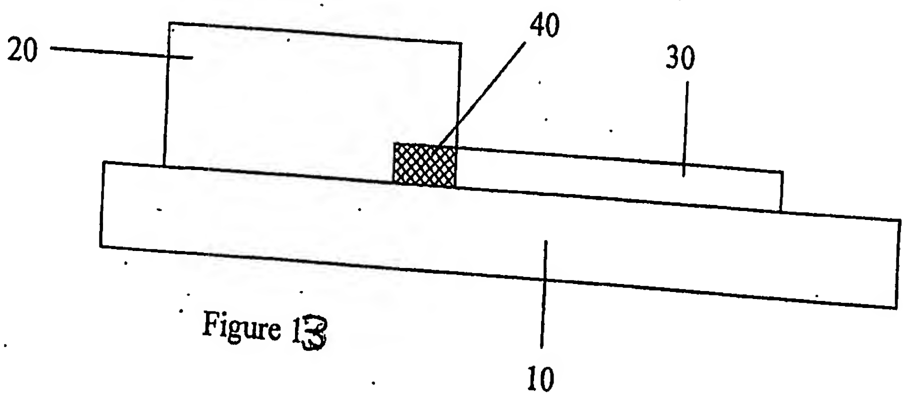

Figure 13

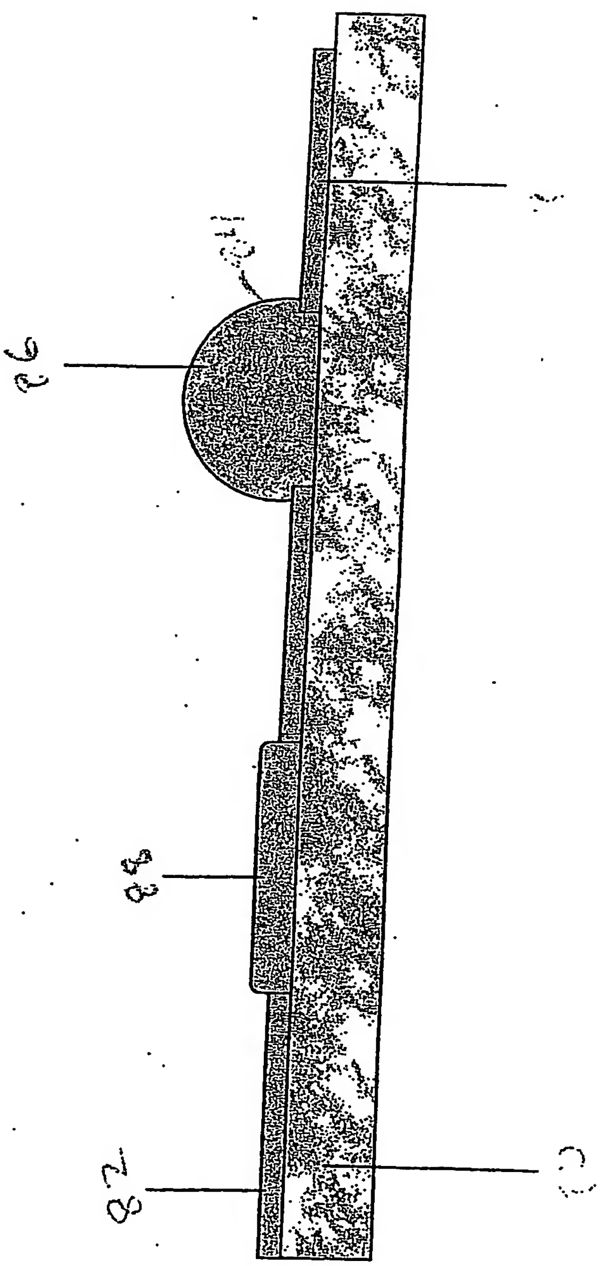

Fig. 14

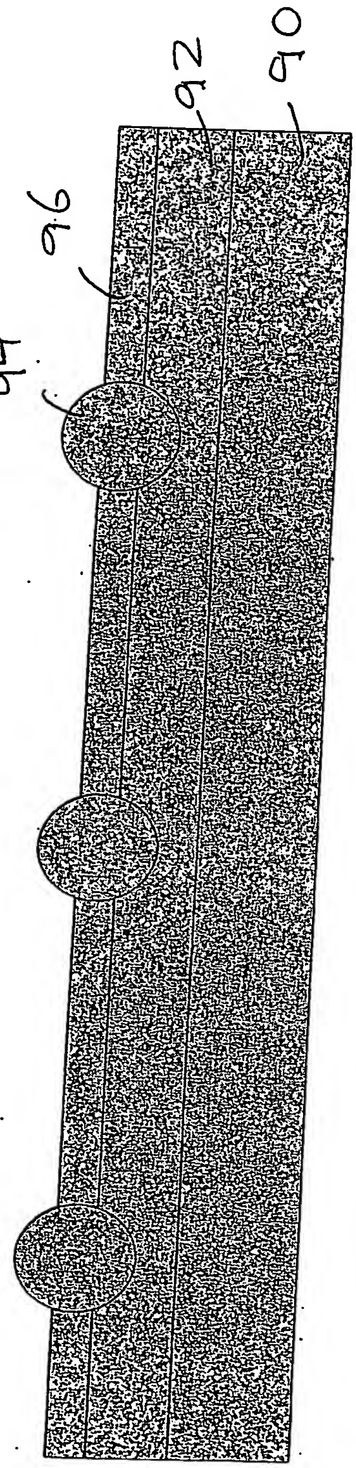

Fig 15

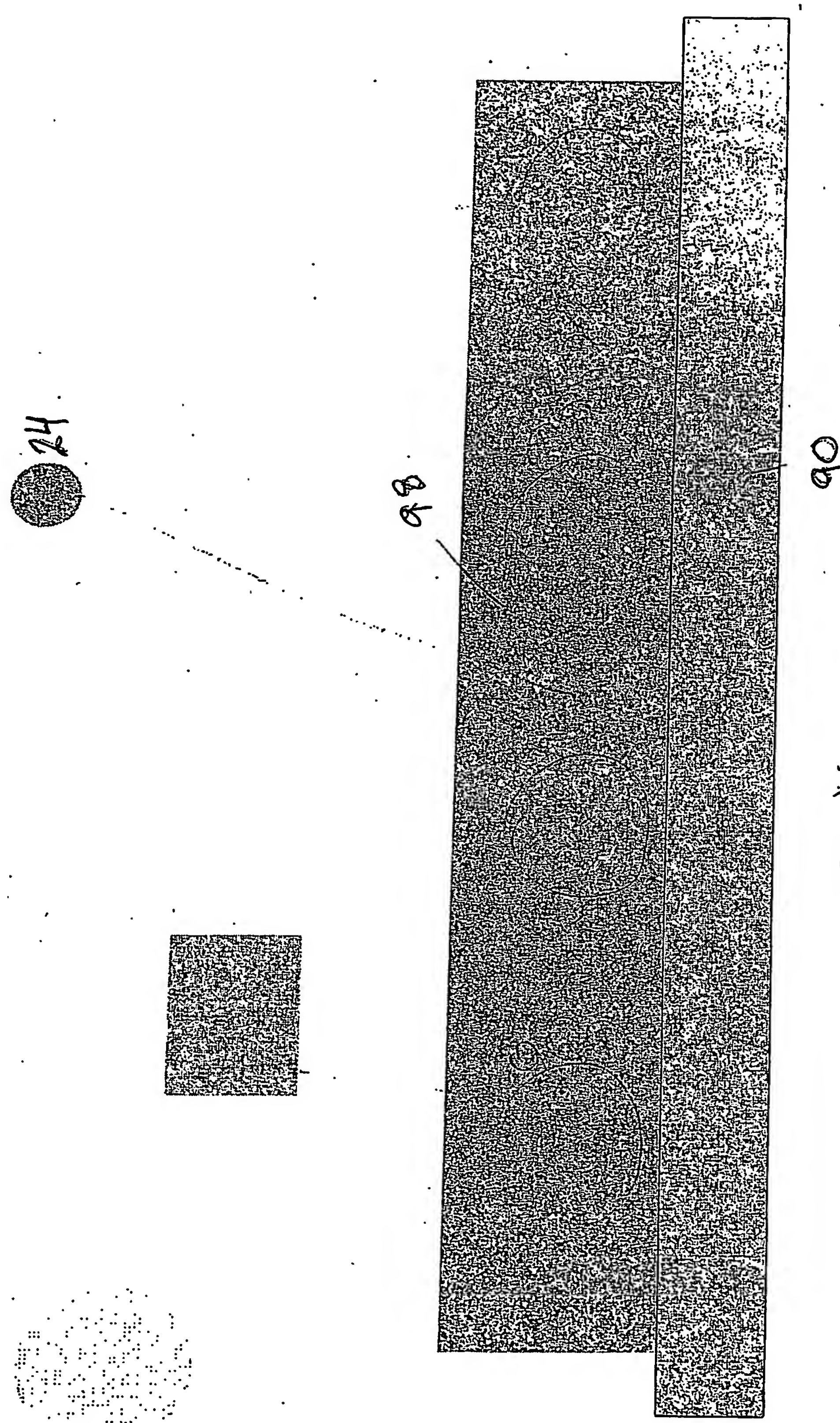

Fig. 16

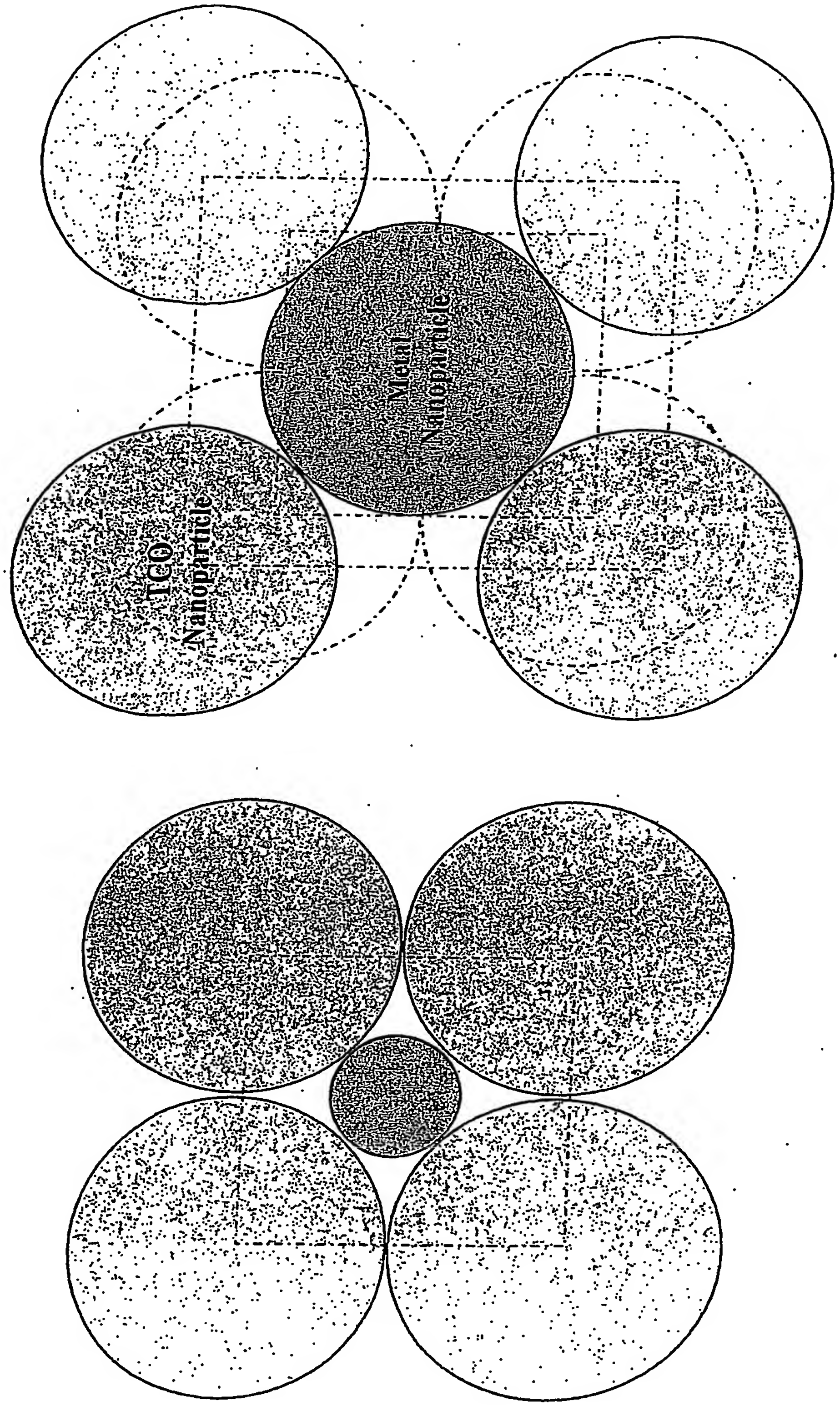

Fig 17